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THE GEOCHEMISTRY AND SOURCE OF SOLUTES IN GROUND WATER FROM THE GLACIAL DRIFT REGIONAL AQUIFER, MICHIGAN BASIN

By

Marc Alan Wahrer

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

THE GEOCHEMISTRY AND SOURCE OF SOLUTES IN GROUND WATER FROM THE GLACIAL DRIFT REGIONAL AQUIFER, MICHIGAN BASIN

By

Marc Alan Wahrer

Ground water from the glacial drift aquifer in the central Lower Peninsula of Michigan has elevated dissolved-solids concentrations (1,000 to 12, 000 mg/L) and isotopically light δ^{18} O signatures (-11.0 to -18.8 ‰) within the Saginaw Lowland Area. The source of the saline water has been hypothesized to be from the upward advection or diffusion of fluids from underlying aquifers and that the likely origin of the isotopically light ground water is from ground water recharged into the basin from glacial melt water during a period when the climate was cooler, such as during the last glaciation of the Pleistocene. The isotopically light, highly saline water has been hypothesized to be due to the slow flushing of the system by present day recharge water. The slow flushing appears to be the result of the presence of relatively impermeable sediments mapped as glaciolacustrine clay.

Stable isotope data indicate the presence of recent and glacial-aged meteoric water. There is also a north-south variation in the distribution of δ^{18} O values reflecting climatic differences in the study area. Dissolved-solids concentrations are generally less than 1,000 mg/L and dissolved chloride concentrations are generally less than 100 mg/L, except in the Saginaw Lowland Area. There are four major hydrochemical facies in the glacial drift aquifer: calcium-bicarbonate, sodium-chloride, calcium-sulfate, and sodiumbicarbonate. Water is generally calcium-bicarbonate, except in the Saginaw Lowland Area where sodium-chloride water is dominant. A significant amount of water-rock interaction is taking place in the glacial-drift deposits and is the most likely source of solutes to the dilute water in the aquifer.

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THE GEOCHEMISTRY AND SOURCE OF SOLUTES IN GROUND WATER FROM THE GLACIAL DRIFT REGIONAL AQUIFER, MICHIGAN BASIN

Chapter 1

INTRODUCTION

INTRODUCTION

During various parts of the hydrologic cycle, natural waters acquire their chemical characteristics. As ground water moves through an aquifer, the chemical composition changes due to dissolution and chemical reactions with mineral constituents and gases, and from mixing with water that has different chemical characteristics (Stumm and Morgan, 1981; Faure, 1991; Drever, 1988; Hem, 1989; Berner and Berner, 1987). Ground water within the glacial drift aquifer in the central Lower Peninsula of Michigan has dissolved-solids concentrations that range from 99 to less than 1,000 mg/L, except in the Saginaw Lowland Area (SLA) where dissolved solids increase to over 12,000 mg/L. In order to determine the major processes controlling the water chemistry within the glacial drift aquifer and solved solids increase to over 12,000 mg/L.

PURPOSE AND SCOPE OF THE RESEARCH

Ground-water has increasingly become an important source of water in the state of Michigan. This increased demand on the ground-water supply has prompted the need for a detailed analysis of ground water within aquifers of the Michigan basin. As part of the Michigan basin Regional Aquifer System Analysis project (RASA), the U. S. Geological Survey began a study to define the hydrologic framework, describe the geochemistry of the ground-water, and analyze the regional ground-water flow patterns within the Michigan basin (Mandle, 1986). The study area for the Michigan basin RASA project covers an area of approximately 29,000 mi² of the Lower Peninsula of Michigan and is bounded by the contact between the Mississippian Coldwater Shale and the overlying Mississippian Marshall Sandstone (fig. 1). This thesis deals with the investigation of the glacial drift aquifer portion of the Michigan basin RASA study. The study area for the focus of this research involves the interpretation of chemical and stable isotope



Figure 1.-Map of the lower Peninsula of Michigan depicting the location of the Michigan basin RASA study area and the boundry of the glacial drift aquifer.

analysis to determine the geochemistry, chemical controls and source for solutes in the ground water from Pleistocene age aquifers in the glacial-drift deposits of the Michigan basin.

Ground water from the glacial drift aquifer is an important source for fresh water in certain areas of Michigan. Water in the glacial drift aquifer has concentrations ranging from fresh (dissolved solids < 500 mg/L) to saline (dissolved solids > 1,000 mg/L). In general, the glacial drift aquifer contains fresh water throughout the study area, with the exception of water from the Saginaw Lowland Area (fig. 2). In parts of the Saginaw Lowland Area, in particular, the water chemistry is unique. Not only is the water unusually saline, but it is also isotopically light. This study was able to examine the geochemical and isotopic data, on a basin wide scale, in an attempt to relate the data to regional ground-water flow. The research also includes a detailed discussion of the geochemistry and the distribution of the major ions and stable isotopes in the ground water from the glacial drift aquifer.

To investigate the chemical and isotope data from the glacial drift aquifer, X-Y plots, frequency histograms, piper diagrams, and distribution maps are used. As discussed by Long et al (1986), each of these techniques addresses different aspects of ground water chemistry and can be used to (1) compare data and water masses, (2) chemically classify water, (3) test hypothesis on chemical and physical controls and (4) study the chemical evolution of a water system.

Chemical equilibrium modeling was used to evaluate the geochemistry of the ground water and determine the relationship between the ground water and the mineralogy. Stable isotope data was used to try and delineate the recharge and discharge areas of the basin and possible age relationships of water masses. This research examined whether the areas mapped as glaciolacustrine clay, in the Saginaw Lowland Area and Michigan Lowland Area (MLA), has effected the chemistry of the ground water in the glacial drift aquifer (fig. 2). A total of 331 chemical analyses and 194 isotope analyses



Figure 2.-Map showing the location of the Saginaw Lowland Area and the Michigan Lowland Area. (modified from Sun, R.J., and Johnston, R.H. in press)

from ground water samples were used to investigate the geochemistry of the glacial drift aquifer.

HYPOTHESIZED CONTROLS ON GLACIAL DRIFT GROUND WATER

The following processes are hypothesized controls that may be affecting the ground-water chemistry within the glacial drift aquifer. In order to determine the chemical controls on the ground water, it is assumed that the various processes leave characteristic geochemical signatures on the water. These geochemical signatures can be the absolute or relative concentrations of the elements or the chemical variations throughout the ground water system (Long and others, 1986).

Water-Rock Interactions

The processes of water-rock (solution-mineral) interactions are driven by the water-rock system attempting to come to a chemical potential equilibrium. The two major interactions that can take place between the solution and mineral are precipitationdissolution and elemental reactions.

The formation of calcite (CaCO₃) and amorphous silica (SiO₂) are examples of precipitation reactions that can occur in ground water. Dissolution reactions can be either congruent or incongruent, but many naturally occurring chemical compounds dissolve congruently. When a mineral dissolves congruently, all ions in the mineral are dissolved and no compounds are formed. A typical example of this type of reaction is the congruent dissolution of halite:

$$NaCl = Na^{+} + Cl^{-}$$
 (1)

However, many minerals that effect the chemical evolution of ground water dissolve incongruently (Freeze and Cherry, 1979), that is, only partial dissolution occurs along with the formation of a new solid compound. An example of this type of reaction is

the incongruent dissolution of the mineral albite to form kaolinite and several dissolved species:

NaAlSi₃O₈(s) + H₂CO₃ +
$$^{9}/_{2}$$
H₂O \leftrightarrow Na⁺ + HCO₃⁻ + 2H₄SiO₄ + $^{1}/_{2}$ H₂Si₂O₅(OH)₄(s)
Albite Kaolinite (2)

The elemental water-rock processes involve adsorption-desorption reactions and exchange reactions. During the precipitation of certain oxides, the reactive oxide surfaces that are formed can adsorb or scavenge cations from solution. Other important adsorbers are clays and organic matter (Long and others, 1986). Adsorption-desorption reactions typically control trace metals in solutions.

Exchange reactions occur when an ion exchanges for another ion in a mineral. This reaction can take place at the surface of the mineral, between the mineral lattice sites, or on the mineral lattice sites (Long and others, 1986). Clay minerals are commonly involved in this kind of reaction process because all clay minerals exhibit ion exchange behavior to some degree (Drever, 1988). Ion-exchange reactions will exert an important control on water chemistry whenever water is in contact with sediments (Drever, 1988). It is very difficult however, to distinguish between exchange reactions and adsorption reactions as controls on an elemental geochemistry (Long and others, 1986).

Microbiological Processes

The microbiological breakdown of organic matter is one control on ground-water chemistry that is many times not investigated. The important microbiological processes and associated reactions are as follows:

fermentation

$$C_{org} + 2H_2O = CO_2 + CH_4$$
 (7)

These reactions are theoretically mutually exclusive, which means that fermentation will not occur until sulfate reduction is completed. Long and others (1986, 1988) have already shown that sulfate reduction is occurring in Bay County, Michigan and this thesis will also investigate whether sulfate reduction has affected other parts of the aquifer.

Anthropogenic Sources

The activities of man can impact the chemistry of ground water through general chemical changes or component-chemical changes (Long and others, 1986). The aquifer chemistry can be affected by its utilization, in that, intense use of ground water can lower the water table or begin to produce a large cone of depression which may bring saline waters into the aquifer contaminating the water supply.

In most cases component-chemical changes are the most common. These changes include the addition of Cl to the ground water from road salt, contamination from an industrial spill or a leaky landfill, acid mine drainage from abandoned coal mines, or introducing fertilizers, pesticides and herbicides to the ground water from farming activities. In the Saginaw Lowland Area, man has pumped ground water, drilled holes for exploration of oil, gas, and brine and mined for coal. Records from the 1890's show that a number of areas in the state have highly mineralized and saline water in the drift, as well as bedrock aquifers. Many of the reports precede the coal mining activity, which took place from 1897 to 1950. This suggests that the highly saline ground waters of the SLA are at least in part from natural processes. Subsurface activities, such as coal mining and disposal of brines associated with the exploration for oil, gas and brine, may have also affected the ground waters in select areas. However, the exploration activities may have only enhanced the natural process of upwelling of brine in the SLA by providing conduits for the saline waters to move up and mix with the freshwater in the overlying aquifers.

Therefore, in localized areas the drilling and mining activities of man may have sped up the natural process of upward migration of brine from below.

Input Controls

Recharge of water into an aquifer, is driven by the attempt of water masses to come to hydrodynamic potential equilibrium (Long and others, 1986). Input can be from meteoric waters and from upward migration of waters from below the aquifer. These recharging waters can have an important effect on the ground water within the aquifer. The chemistry of the water can also be effected by mixing of water masses such as, mixing between freshwater and brine. However, the types of geologic material in the system, play a large role in ground water recharge. In certain areas clays may deter recharge or ground water movement, while in other areas where less clay exists, water could more easily recharge the aquifer. Other physical processes may also effect recharge. In the Michigan basin, the ground-water system may still be readjusting to the effects of the Pleistocene glaciations and still working back towards equilibrium.

PAST WORKS

Geochemical analyses of ground water in glaciated systems have received considerable interest in recent years through work by Newbury et al. (1969); Cherry (1972); Sklash et al. (1976); Desaulniers and others (1981); Wallick (1981); Bradbury (1984); Hendry et al. (1986); Handy (1982); Siegel and Mandle (1984); Twenter and Cummings (1985); Long and others (1986, 1988, 1993); Wilson and Long (1990) and Kenoyer and Bowser (1992). Through these works, a number of significant contributions have been made in the understanding of the evolution of ground water in glaciated areas.

Early studies by Wallick (1981) and Cherry (1972) were able to characterize the chemical evolution of ground water in glaciated drainage basins by observing the influence of water-rock interactions on major ions in ground water. Vander Berg and Lennox

(1969) considered base-exchange, sulfate reduction and membrane-filtration processes to be important in the chemical evolution of ground-water in south-central Alberta (Wallick, 1981). Work by Hendry et al., (1986) indicated that high sulfate concentrations in fractured weathered till in Alberta was mainly due to the oxidation of organic sulfur by bacteria, along with the dissolution of minor amounts of sulfate-rich bedrock materials.

In North America, the chemical composition of most natural ground waters derived from glaciation may be broadly categorized into three types (Freeze and Cherry, 1979). Type I waters are characterized by slightly acidic water with dissolved-solid concentrations < 1,000 mg/L with Na⁺, Ca⁺² and/or Mg⁺² and HCO₃⁻ as the dominant constituents in solution. The chemical evolution of this water is thought to be controlled by the interactions with aluminosilicate minerals (Freeze and Cherry, 1979). Type II waters are characterized by slightly alkaline water with dissolved-solid concentrations < 1,000 mg/L with Ca⁺ Mg⁺², and HCO₃⁻ as the dominant species in solution. Freeze and Cherry (1979) suggest that these waters are primarily the result of carbonate mineral dissolution under open or partially open system CO₂ conditions. Type III waters are characterized by slightly alkaline brackish waters with dissolved-solid concentrations ranging from 1,000 to 10,000 mg/L with Na⁺, Ca⁺², Mg⁺², HCO₃⁻, and SO₄²⁻ as the dominant species in solution. Type III waters are thought to be derived from the dissolution of evaporites, and carbonates.

Ground water from the glacial drift aquifer in the Michigan basin would fall into the Type II and Type III water categories. The ground water within the Saginaw Lowland Area (fig. 2) would be classified as Type III waters with elevated chloride concentrations. In this area of the aquifer the ground water has dissolved-solids concentrations of greater than 1,000 mg/L and is generally a Na-Cl facies. The ground water in the rest of the glacial drift aquifer would be classified as Type II waters. Dissolved-solids concentrations in these areas are less than 1,000 mg/L and the hydrochemical facies is generally Ca-HCO₃.

Early work focusing on the Lower Peninsula of Michigan revealed the existence of brine springs (Houghton, 1838; Winchell, 1861). High saline water was recognized and mapped in the Saginaw and Erie Lowlands in glacial drift and near-surface bedrock aquifers by Lane (1899) (fig 3). Twenter (1966) mapped saline water in the Michigan Lowland Area as well as the Saginaw and Erie Lowlands (fig. 3). The saline water in the Saginaw Lowland Area, located in the east-central Lower Peninsula of Michigan, has been the focus of many investigations (Mandle and Westjohn, 1989; Mandle, 1986; Long and others, 1986,1988,1992, 1993; Badalamenti, 1992; Meissner et al., 1992; Meissner, 1993; Wahrer et al., 1992; Wahrer, 1993). The area is unique, in that saline ground water is found in near-surface bedrock aquifers, as well as, the glacial drift aquifer. The glacial drift aquifer contains saline ground water with dissolved-solids concentrations greater than 1,000 mg/L. The ground water has also been shown to be enriched in Ca, Mg, Na, Cl, Fe, and SO4 (Handy, 1982; Twenter and Cummings, 1985).

Work by Long and others (1986) has shown that the ground water in this area is not only saline but also isotopically light (fig. 4). The saline water was attributed to the upward advection and/or diffusion of solutes from below. The isotopically light meteoric water was attributed to ground water recharged to the aquifer when the climate was cooler, such as during recent glaciation. This conclusion is consistent with the results of Desauliniers and others (1981) for pore water in argillaceous deposits in southwestern Ontario and of Siegel and Mandle (1984) for the Cambrian-Ordovician aquifer in the North-Central United States. Sulfate reduction was also shown to be occurring in the area affecting SO₄ and HCO₃ concentrations as well as δ^{34} S and δ^{13} C values.

Badalamenti (1992) studied ground water derived from near-surface deposits of the SLA and incorporated the study area of Long et al, 1986 (fig. 5). Badalamenti found that there was a correspondence in geographic distribution of light δ^{18} O and δ D values, high chloride concentrations, surficial lacustrine and morainal clay deposits, and the





Area where dissolved solids in shallow bedrock units is > 1,000 (Twenter, 1966).



Area where shallow ground water is highly mineralized (Lane, 1899).

Figure 3.-Map showing the area where shallow ground water is highly mineralized (Lane, 1899) and area where dissolved solids in ground water in shallow bedrock units exceeds 1,000 mg/L (Twenter, 1966).



Figure 4.-Map showing the study area of Long et al., 1986 and 1988.



Figure 5.-Map showing the study area of Badalementi, 1992.

residual potentiometric surface. She also concluded that the regional ground water system is influenced by meteoric water and brine end members.

Although Long and others (1986, 1988) have also hypothesized that the source of the high solutes in the glacial drift and near-surface-bedrock aquifers is from the upward advection or diffusion of fluids from below, the source for these solutes was not known. Therefore, the purpose of this thesis is to determine the geochemistry and source of solutes in ground water from the glacial drift regional aquifer. This thesis also compares the geochemistries of the ground water in the aquifer, to the ground-water chemistry of the underlying aquifers in the Michigan basin.

CHAPTER 2

GEOHYDROLOGIC FRAMEWORK

GEOHYDROLOGIC FRAMEWORK

STUDY AREA

The Michigan Basin is a nearly circular basin that includes an extensive accumulation of sedimentary rocks that underlie the Lower Peninsula of Michigan and parts of Michigan's Upper Peninsula, Wisconsin, Illinois, Indiana, Ohio, and Ontario, Canada. It is bounded by the Canadian Shield on the North, by the Wisconsin dome and Wisconsin arch on the Northwest and West; by the Kankakee arch on the Southwest; and by the Algonquin and Findlay arches on the East and Southeast (Mandle, 1986; Cohee, 1965) (fig. 6).

Within the Michigan basin, rocks of Precambrian through Jurassic age locally exceed 17,500 feet in thickness and overlie Precambrian crystalline rocks (Lillienthal, 1978). Part of the Mesozoic sequence including the Triassic, Lower and Middle Jurassic and Cretaceous strata, is missing. The entire sequence of Paleozoic through Mesozoic rocks is mantled by glacial drift-deposits which range from a few inches to about 1,000 feet in thickness (Mandle, 1986). These glacial deposits were deposited during the Wisconsin and probably earlier glaciations. The glacial and Holocene deposits are the only Cenozoic sediments found within the Michigan basin.

AQUIFERS

The RASA study area consists of four major aquifers that include the glacial drift, Grand River-Saginaw, Parma-Bayport, and the Marshall. The stratigraphic and hydrologic relationship among the units within the Michigan basin are shown in figure 7. The bedrock portion of the aquifer system consists of 3 aquifers and 3 confining units. The Coldwater Shale forms the bottom portion of the aquifer system and consists of shale that ranges from 500 to 1,100 ft in thickness. The oldest aquifer within the RASA study area is the Mississippian aged Marshall Sandstone aquifer. The Marshall aquifer includes





Era	Period	Epoch	Glaciation		Stratigr	Hydrogeologic Unit	
oic.	nary	Holocene					Glacial drift
Cenoz	Quater	leistocene	Wisconsin Illinoian Pre-Illinoian				aquifers
Mesozoic	Jurassic	Late		Ur	named Id beds		Glacial till-red beds confining unit
	vanian	Middle		Grand Ri	iver Formation		Grand River-Saginaw aquiter
	Pennsy	Saginaw Formatic	w Formation	Seginaw c Parma Sandstone Member	Seginaw confining unit		
zoic		ate		Grand Rapids Group	Bayport Limestone		Parma-Bayport aquifer Michigan confining unit
Pale	Isippian	_		Marshal	Formation Sandstone	Stray Sandstone Member Napoleon Sandstone Member	Marshall aquifer
	Missi	Early		Coldue	iter Shale		.Coldwater confining unit

Figure 7--Chart showing stratigraphic and hydrologic units of the study area (Modified from Mandle and Westjohn, 1989, fig. 3; stratigraphic column modified from Michigan Department of Conservation, Chart 1, 1964) Michigan basin. sandstones that overlie the Coldwater confining unit and sandstones that form the lower part of the Michigan Formation. The Marshall aquifer consists of two or more permeable sandstones in the central part of the basin. In these areas intercalated carbonate, shale, siltstone, and/or evaporite separate the permeable sandstone. The aquifer consists of one permeable sandstone toward the subcrop regions. The composite thickness of the permeable sandstone ranges from approximately 75 to 225 ft.

Overlying the Marshall aquifer, and separating it from the Parma-Bayport aquifer, is the Michigan confining unit. This unit consists of an intercalated sequence of thin bedded limestone, dolomite, shale, gypsum, anhydrite, and lenses of sandstone. The Michigan confining unit ranges in thickness from 100 ft near the fringes of the subcrop area to about 400 ft over the central part of the study area (D.B. Westjohn, written communication, 1991).

Overlying the Michigan confining unit is the Parma-Bayport aquifer, which is Pennsylvanian/Mississippian in age. This aquifer consists of both the Parma Sandstone and the Bayport Limestone and ranges from 75 to 150 ft in thickness (D.B. Westjohn, written commun., 1991). In areas where the Bayport Limestone is absent the Parma Sandstone is present and overlies the Michigan confining unit. The Parma Sandstone contains sandstone, shale, siltstone, and thin lenses of limestone (Cohee, 1965). The Bayport Limestone is predominantly sandstone, sandy limestone, and limestone (Cohee, 1965). Overlying the Parma-Bayport aquifer is a shale comprising the Saginaw confining unit.

Overlying the Saginaw confining unit is the Pennsylvanian aged Grand River-Saginaw aquifer. These Pennsylvanian aged rocks have been subdivided into the Saginaw (Early Pennsylvanian) and the Grand River Formations (Late Pennsylvanian). Pennsylvanian sandstones are stratigraphically discontinuous and only locally constitute the dominate lithology. Shale, siltstone, limestone, and coal are minor contributors of the total thickness of the Pennsylvanian bedrock sequence. In the east-central part of the

basin, where Pennsylvanian rocks are the thickest (600 to 700 ft), the composite thickness of sandstones ranges from 300 to 400 ft. However, the composite thickness of the sandstones that comprise the Grand River-Saginaw aquifer is less than 200 ft over most of the basin (D.B. Westjohn, personal communication, 1992).

During the Mesozoic and early Cenozoic Eras an eroded bedrock surface was developed and sediments briefly accumulated during the Late Jurassic and Late Cenozoic Eras. Upper Jurassic Red Beds, which are found overlying the Pennsylvanian units, in the west-central part of the study area, are dominantly composed of red muds, poorly consolidated red shale, gypsum, and minor amounts of sandstone. These deposits, along with fine-grained lacustrine clay and till, form the glacial till-red beds confining layer (Mandle and Westjohn, 1989). The surficial aquifer of the study area is the glacial drift aquifer that is Pleistocene in age. The glacial drift aquifer is the focus of this thesis and a detailed discussion of the geology of this aquifer will be presented in the following section.

GLACIAL GEOLOGY

A cover of glacial drift, alluvium, and lake sediments, mainly of Pleistocene age, mantles nearly the entire study area (fig. 8). The drift deposits are thickest in the north and central parts of the Michigan basin and become thinner to the South. The deposits range in thickness from 600 to 1,000 feet in the northern part and from 10 to 200 feet in the southern part (Western Michigan University, 1981, plate 15). In the central portion of the study area glacial deposits generally range from 200 to 400 feet in thickness. The glacial deposits include lacustrine clay, till, and glaciofluvial deposits. The texture of the glacial drift deposits range from a fine-grained lacustrine clay or till, to coarse-grained outwash deposits and till. In the northern and northwestern parts of the study area, where coarse-grained glacial deposits dominate, they are productive aquifers. Where finedgrained deposits dominate, such as the SLA, the glacial deposits are not productive aquifers and often form confining units (fig. 8).


Figure 8--Map showing Glacial-drift deposits in Michigan's Lower Peninsula (Modified from the Glacial Map of the United States east of the Rocky Mountains, Geological Society of America, 1959). A surficial map of the Pleistocene glacial deposits of Michigan was published by Martin (1955). Many investigators have since revised this map, but Farrand and Bell (1984) provided a map in which they have differentiated lithologies of the surficial glacial deposits. However, at this time no large-scale map differentiating the drift lithologies in the subsurface has been produced. From the data available, regional stratigraphic trends cannot be recognized within the drift, which probably reflects the heterogeneity and complex depositional history of the glacial deposits. For the purpose of this study, the glacial deposits are considered a single aquifer unit called the glacial drift aquifer.

In a study of Garfield township in Bay County, Chittrayanont (1978) identified the minerals illite, kaolinite, chlorite, quartz, feldspar, calcite and dolomite in the glacial-drift deposits. Gypsum is also heterogeneously distributed throughout the glacial deposits (Wood, 1969). Several hydraulic properties were also measured for the glacial drift aquifer. Transmissivity values for 109 aquifer tests conducted in wells in the glacial drift ranged from 650 to 82,000 ft^2/d (Reed and others, 1966; Michigan Department of Public Health, Engineering Division, written communication, 1987; Michigan Department of Natural Resources, Geological Survey Division, written communication, 1987). Values for horizontal hydraulic conductivity range from less than 50 to more than 500 ft/d.

HYDROLOGIC SETTING AND GROUND-WATER FLOW

The Lower Peninsula of Michigan is surrounded by three of the Great Lakes, Michigan, Huron and Erie (fig. 6). Lake Michigan is located on the western side of the Peninsula, Lake Huron on the eastern and northeastern sides, and Lake Erie on the southeastern side. A surface water drainage divide, formed in part by glaciation of the Peninsula, runs north to south and divides the Peninsula approximately in half (Mandle, 1986). This divide allows rivers on the western half of the Peninsula to drain into Lake Michigan while the rivers on the eastern half of the Peninsula drain into Lake Huron and Lake Erie.

A ground-water drainage divide nearly parallels the surface-water drainage divide which runs roughly north-south and divides the Lower Peninsula of Michigan into two drainage basins of approximately equal areal extent (Grannemann, personal comm., 1991). This divide is formed, in part, from the interlobate and end-moraine deposits that formed between the Michigan and Saginaw ice lobes.

On a regional scale, the water table mimics the topography of the Lower Peninsula (Mandle, 1986). A water table map of the Lower Peninsula shows the presence of two areas of relatively high water-table altitude in which separate, sub-regional flow systems are assumed to exist; these are the northern and southern upland areas (Mandle and Westjohn, 1989) (fig. 9). The water table slopes away from the Upland areas either toward the Great Lakes, or toward an elongated northeast-southwest trending depression in the water table. This depression is located in the pro-glacial Grand River Valley, the site of the present-day Grand, Maple, and Saginaw Rivers. Generalized ground-water flow directions (fig. 9) show that water in the glacial drift aquifer moves from upland areas down gradient to lowland areas (Mandle and Westjohn, 1989). Most upland area recharge discharges to streams along local flow paths. The rest infiltrates into the glacial drift aquifer and moves along intermediate and regional flow paths toward discharge areas such as the Saginaw Bay Area or Michigan Lowlands Area. Most water in the Glacialdrift aquifer discharges to streams that drain to Lakes Michigan, Huron, or Erie (Grannemann, written communication, 1992). A small amount of ground water discharges from the glacial drift aquifer directly to the lakes or channels connecting the lakes.

PRECIPITATION DATA

The average annual precipitation over Michigan is approximately 31 inches (Michigan Department of Agriculture Michigan Weather Service, 1974). In nature usually much of this water is lost by evaporation, transpiration, and surface runoff before it enters



Figure 9--Map showing water table and generalized ground-water-flow directions for the Glacial-drift aquifer in the Lower Peninsula of Michigan (Modified from Mandle and Westjohn, 1989). the ground-water reservoirs. The amount of precipitation that enters the ground-water reservoirs in any area is influenced by numerous factors; the duration, intensity, and type of precipitation; the density and types of vegetation; the topography; and the porosity, permeability, and the degree of saturation of the soil, subsoil, and underlying rock formations (Giroux and Thompson, 1959). The mean precipitation and mean snowfall in inches for the Lower Peninsula of Michigan are shown in figure 10. These maps show areas were large amounts of precipitation and snow may affect the ground-water chemistries in recharge areas.

HISTORY OF RECENT GLACIATION WITHIN THE MICHIGAN BASIN

The Pleistocene epoch in North America lasted nearly 2,000,000 years and was characterized by four episodes of glaciation, during which time, large areas of Canada and the United States were scoured and covered by thick ice sheets. In Michigan, there is evidence only for the last ice advance of the Wisconsinan. Earlier ice advances during the Illinoian, Kansan, and Nebraskan have not been identified and have probably been eroded, reworked and incorporated into the younger Wisconsinan deposits.

The chronology of the Wisconsinan (110,000 to 10,000 years BP) consists of Early Wisconsinan, Middle Wisconsinan, and Late Wisconsinan. The events of the Early Wisconsinan (110,000 to 55,000 years BP) are unknown in Michigan due to the lack of exposure or presence of deposits from that time (Eschman, 1985). Evidence from interglacial sediments found in Michigan and Canada suggests during most of the Middle Wisconsinan (55,000 to 24,000 years BP) Michigan was relatively free of ice (Eschman, 1985).

Most of the glacial features found in the Michigan basin were formed during the Late Wisconsinan (24,000 to 10,000 years BP) which was marked by four major episodes of ice advance (Eschman, 1985). Ice advances and retreats account for a complex physiography of glacial lake deposits, moraines, drumlins, eskers, outwash plains, and





glacial drift that ranges from 0 to 1000 ft in thickness (Fisher and Others, 1988). The four sub-stages of the Late Wisconsinan in this area are the Nissouri (21,000 years BP), Port Bruce (15,500 years BP), Port Huron (13,000 years BP) and Greatlakean (11,500 years BP) (Mandle, 1986; Eschman, 1985; Fullerton, 1980). The maximum ice advance for each sub-stage is shown in figure 11. The oldest sub-stage, Nissouri, advanced the farthest as it completely covered the Lower Peninsula and reached parts of Ohio and Indiana. Each of the successively younger sub-stages did not advance as far south as the previous one, with the final sub-stage, the Greatlakean, only advancing to the tip of the Lower Peninsula. According to Broecker and Farrand (1963), approximately 10,000 years ago the ice from the last glaciation receded from Michigan.

During much of the Wisconsinan glacial the ice margin was well south of the state, and all of Michigan was covered by several thousand feet of ice (Dorr and Eschman, 1970). Each ice advance and retreat greatly altered the physiography of the Michigan basin by continued scouring of the bedrock. The eroded bedrock surface apparently included a surface-drainage network located in large valleys in the general vicinity of the present Great Lakes (Hough, 1958; Mandle, 1986). As a result of continued ice advances, the pre-glacial valleys became more pronounced. The presence of these pre-glacial valleys and the surrounding, more resistant, bedrock uplands created pathways for subsequent glacial ice advances, and is the most likely reason for the highly lobate character of the late Wisconsinan ice advances (Horberg and Anderson, 1956; Hough, 1958; Eschman, 1985; and, Mandle and Westjohn, 1989). Figure 12 shows the control that the major, preexisting topographic features of the Great Lakes Region exerted on the shape of the ice front (Dorr and Eschman, 1970). It is also noteworthy that the end moraines are looped around each of the several major lowlands now occupied by Lake Superior, Lake Michigan, lakes Huron and Erie, and Saginaw Bay (Dorr and Eschman, 1970).



Figure 11--Map showing the highly lobate character of the Late Wisconsinan ice advances (from Mandle and Westjohn, 1989; modified from Wayne and Zumberge, 1965).



Figure 12--Map showing the four maximum ice advances during the Late Wisconsinan (from Mandle, 1986; Eschman, 1985).

Chapter 3

METHODS OF DATA COLLECTION AND REDUCTION

METHODS OF DATA COLLECTION AND REDUCTION

SAMPLING

A total of (331) ground-water samples, collected from the glacial drift aquifer, are used in this research. Figure 13 shows the glacial drift aquifer study area and distribution of sample locations where chemical analyses are available. Chemical data was collected from all 331 samples and 194 samples were analyzed for isotopes of oxygen and hydrogen. Ground-water samples were taken from (183) wells in the glacial drift aquifer of the Michigan basin as part of the Michigan RASA project (Dannemiller and Baltusis, 1990). In addition to the data collected for this study, chemical data utilized in this thesis were obtained from Wood (1969) (37 samples), Long and others (1986) (39 samples), Michigan Department of Public Health (written communication, Mark Breithart, 1992) (29 samples), and the U.S. Geological Survey <u>WAT</u>er Data <u>STO</u>rage and <u>RE</u>trieval System (WATSTORE) database (43 samples). Further sampling was completed during the summer of 1991 with the objective of supplementing the isotope data for the aquifers. Nineteen ground-water samples were taken which included measuring for 18/16O, 13/12C, 34/32S, and 14C.

ANALYTICAL METHODS

Ground-water sample locations were selected on the basis of well location, depth, open interval, pumping equipment, aquifer type, and lithology (Dannemiller and Baltusis, 1990). Nearly all of the samples were taken from municipal and domestic wells for which drillers logs were available. Prior to collecting the ground-water samples, the wells were pumped until temperature and specific conductance remained constant. At each well site, field measurements for specific conductance, pH, and temperature were determined, as well as concentrations of dissolved oxygen, alkalinity (CaCO₃), sulfide, total iron, and ferrous iron. Analysis of the samples included measurements for parameters used for



Figure 13--Map showing the location of ground water sampling sites for the glacial drift aquifer.

geochemical modeling. The methods for measuring and analyzing ground water at the well site are shown in table 1.

Ground-water samples were also analyzed for 8 major and 18 minor inorganic constituents. The 8 major inorganic constituents that were analyzed include; Ca, Mg, Na, K, Cl, SO₄, F, and Br. The 18 minor inorganic constituents include; Si as SiO₂, Al, As, Ba, B, NO₂, NO₂ + NO₃, Fe, Ferrous, Li, Mn, Sr, Zn, residue on evaporation (R.O.E.), dissolved organic carbon (D.O.C.), and stable isotopes of 18O/16O, 2H/1H, 34S/32S, 13C/12C, percent 14C and total Tritium (³H). All ground-water samples were not analyzed for all of the species listed above. For example, much of the historical data had no isotope analyses or incomplete chemical analyses.

The procedure for collecting ground-water samples included filtering them through a membrane (Geotech filter) using a pore size of 0.45 micrometers. In order to minimize the exposure of the sample to the atmosphere, the discharge from the well pump was diverted into the filter through a continuous flow line. Water samples were preserved according to the methods described in Brown and others (1970) and Skougstad and others (1978). The water samples were then analyzed by the U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado.

DATA REDUCTION TECHNIQUES

In order to more effectively interpret the ground water analyses, several data reduction techniques are used. These techniques include preparing Piper diagrams, spatial distribution maps, x-y plots, general statistic tables, and frequency histograms for both the chemical species and stable isotopes. Piper diagrams and spatial distribution maps have been prepared using computer programs on the U.S. Geological Survey Prime computer system. Frequency histograms and x-y plots have been constructed and modified using the programs STATGRAPHICS version 5.0 and FREELANCE GRAPHICS version 4.0. The data was chemically modeled using the computer code WATEQ4F (Ball et al, 1991).

Table 1 Methods of measuring and analysing ground water at the well site
(from Dannemiller and Baltusis, 1990)

Property or Constituent	Measurement or analytical method
Temperature, in degress Celcius	Recorded during specific-conductance measurement by use of thermister in specific-conductance probe. Probe calibrated with a certified mercury thermometer (Wood, 1976, p. 10).
Specific conductance, in microsiemens per centimeter at 25 degrees Celsius	Specific-conductance meter calibrated with standards obtained from U.S. Geological Survey Naional Water Quality Laboratory. Results were temperature corrected by use of the following correction factor, where (T) is measured in degrees Celsius:correction factor = $1/1+[0.2(T-25)]$
рН	pH meter calibrated with two standard solutions (pH 4.00 and 7.00). Samples water kept at its original temperature during measurement by means of a water bath.
Alkalinity (bicarbonate), in milligrams per liter	Potentiometric titration with 0.01639N H_2SO_4 through end inflection points. Centroid of the inflection point was graphically determined (Stumm and Morgan, 1981). Sample water kept at original temperature during measurement by means of a water bath.
Dissolved oxygen, in milligrams per liter	Azide modification of Winkler method used (Hach Chemical Co., 1987). Sample kept frm exposureto the atmosphere during collection. The sample bottle was filled by submerging it in a water bath of sample water, filling the bottle from a hose connected to the well pump, and capping the bottle while it was still submerged.
Ferrous iron (Fe ²⁺), in micrograms per liter	1, 10-phenanthroline method used (Hach Chemical Co., 1987). Sample kept from exposure to atmosphere before analysis by collecting it from the well's discharge line with a syringe.
Total iron (Fe), in micrograms per liter	Ferrozine method used (Hach Chemical Co., 1987).
Sulfide (S ²⁻), in milligrams per liter	Methylene blue method used (Hach Chemical Co., 1987). Sample kept from exposure to atmosphere before analysis by collecting it from the well's discharge line with a syringe.

Through chemical modeling, saturation indices and activities have been calculated for the waters in the glacial drift aquifer.

Chapter 4

GEOCHEMICAL DISTRIBUTION MAPS

GEOCHEMICAL DISTRIBUTION MAPS

INTRODUCTION

Geochemical data from the glacial drift aquifer was used to prepare maps showing areal distributions of dissolved solids, dissolved chloride, dissolved total iron, dissolved sulfate, and hydrochemical facies for the ground water in the aquifer. These maps and the interpretations concluded from them are based on work by Wahrer et al., (1993), as part of the U. S. Geological Survey's RASA project. The maps were constructed to provide a general distribution and discussion of the selected constituents and the trends, patterns, and gradients that were interpreted from the maps. The chemical data collected provide sufficient coverage for maps prepared from the glacial drift aquifer with the exception of the far eastern and far northeastern portions of the study area where no data was available for the aquifer. Chemical data used to construct these maps were derived from various well depths in the glacial drift aquifer, and therefore only represent general distribution patterns of dissolved constituents and hydrochemical facies. For this section, the Saginaw Bay Area refers to the area in the east central part of the Michigan basin, bound by the outermost moraine of the Port Huron Morainic system, within the SLA (fig. 8).

DISSOLVED-SOLIDS

A map of dissolved-solids concentrations was prepared for water from the glacial drift aquifer (fig. 14). The concentrations were determined by summing the major cation and anion species from analysis of each water sample. Dissolved-solids concentrations range from 99 to 12,214 mg/L with a geometric mean of 630 mg/L. In general, the concentrations increase from the outer parts of the study area toward the Saginaw Bay Area (fig. 14). Dissolved-solids concentrations in water from parts of the Saginaw Bay Area range from 500 to 12,214 mg/L. The area of high dissolved-solids (> 1,000 mg/L) also extends south and to the west away from the Saginaw Bay Area. There is also a thin



Figure 14.-Distribution of dissolved solids in water from the glacial drift aquifer in the lower Peninsula of Michigan (from Wahrer et al., 1993)

band that extends from the center of the basin toward the Michigan Lowlands Area that has water with higher dissolved solids. Most dissolved-solids concentrations in this band range from 500 to 1,000 mg/L, however, one sample had a concentration of 1,171 mg/L. The sources for the high dissolved solids could be due to the dissolution of halite (NaCl), gypsum (CaSO₄•2H₂O) and anhydrite (CaSO₄), or through the mixing of meteoric water and formation brine from underlying bedrock aquifers. The concentrated water of the SLA is hypothesized to be from the result of upward advection or diffusion of fluids from below (Long and others, 1988).

DISSOLVED CHLORIDE

Dissolved chloride concentrations in water from the glacial drift aquifer range from 1 to 6,714 mg/L with a geometric mean of 19 mg/L. Water from most of the study area has a chloride concentration less than 100 mg/L (fig. 15). Chloride concentrations generally increase from the outer parts of the aquifer to the Saginaw Bay Area, where concentrations are as high as 6,714 mg/L. Chloride concentrations between 100 and 1,000 mg/L also occur to the south and to the west of the Saginaw Bay Area. Water with a chloride concentration less than 10 mg/L is probably of recent meteoric origin. The source of the more saline water in the Saginaw Bay Area could be from the upward advection or diffusion of ions in water from the underlying bedrock formations that are mixing with more recent meteoric water (Long and others, 1988). Another possible source for the saline water may be the dissolution of halite, which may be incorporated in the glacial-drift deposits (Wood, 1969).

TOTAL DISSOLVED IRON

Total dissolved iron concentrations in water from the glacial drift aquifer range from 0.001 to 6.0 mg/L (fig. 16) with a geometric mean of 0.301 mg/L. Total iron concentrations represent the combined concentrations of Fe^{+2} and Fe^{+3} . Iron



Figure 15.-Distribution of dissolved chloride in water from the glacial drift aquifer in the lower Peninsula of Michigan (from Wahrer et al., 1993).



Figure 16.-Distribution of total iron in water from the glacial drift aquifer in the lower Peninsula of Michigan (from Wahrer et al., 1993).

concentrations less than 0.1 mg/L occur in the northern fringe of the study area and, to a greater extent, in the northwestern portion of the study area. There are also several small localized areas where ground water contains iron concentrations less than 0.1 mg/L.

Iron concentrations greater than 1 mg/L occur in a large band that extends across the southern part of the study area from the southern part of the Saginaw Bay Area to the Michigan Lowland Area. Most of the southeastern portion of the study area has iron concentrations greater than 1 mg/L. There are also two local areas near the Saginaw Bay Area with iron concentrations above 1 mg/L. Iron concentrations between 0.1 and 1 mg/L occur in ground water in the eastern and southern fringes and in the central and north central parts of the study area. There are also several local areas within the Saginaw Bay Area where concentrations are between 0.1 and 1 mg/L.

DISSOLVED SULFATE

Dissolved sulfate concentrations in water from the glacial drift aquifer range from 1 to 1,800 mg/L (fig. 17) with a geometric mean of 41 mg/L. For most of the study area, sulfate concentrations range from 10 to 100 mg/L. In the northern and eastern fringe areas and the northwestern part of the study area, sulfate concentrations are less than 10 mg/L. There is also a small local area in part of the Saginaw Bay Area where sulfate concentrations are less than 10 mg/L. This area is surrounded by an area where sulfate concentrations range from 10 to 100 mg/L and extends out toward the center of the aquifer. In the northern and southern parts of the Saginaw Bay Area, there are two large areas where water from the glacial-drift aquifer has sulfate concentrations between 100 and 1,000 mg/L. These areas extend to the Southwest and to the West of the Saginaw Bay Area.

The high sulfate concentrations may be due to the influence of water with higher sulfate concentrations from underlying aquifers and ground-water flow directions in the Saginaw Bay Area (fig. 9) (Wahrer et al., 1993). High sulfate concentrations may also be



Figure 17.-Distribution of dissolved sulfate in water from the glacial drift aquifer in the lower Peninsula of Michigan (from Wahrer et al., 1993)

due to the dissolution of gypsum (CaSO₄•2H₂O) and anhydrite (CaSO₄), which are believed to be unevenly deposited in the glacial-drift deposits (Wood, 1969). The areas where ground-water has low sulfate concentrations could be the result of sulfate reduction. Long and others (1988) have shown that, within the Saginaw Bay Area microbial reduction of SO₄²⁻ is occurring. This affects the concentrations of SO₄²⁻ and HCO₃⁻.

HYDROCHEMICAL FACIES AND PIPER DIAGRAMS

The concept of hydrochemical facies is a means of describing the diagnostic chemical character of water (Back, 1961). Piper (1944) developed a diagram, commonly referred to as a Piper plot, that enables the classification of waters using six chemical components that allows easy visual chemical comparisons of water samples, identification of water masses, determination of mixing among water masses, and determination of the chemical evolution of ground water. The chemical components used consist of three cationic Ca, Mg, and Na+K and three anionic Cl, HCO₃+CO₃, and SO₄ species or groups of species as these ions account for the electrical balance in most natural waters (Hem, 1989). Construction of the diagram entails converting cation and anion concentrations to units of milliequivalents/liter and then calculating relative percentages of the cation and anion species or groups of species. The cations and anions each sum to 100%. Each sample is plotted on respective cation and anion ternary diagrams and also on a central diamond-shaped diagram (fig. 18a). The sample location on the diamond diagram is determined by the intersection of projections from its position in the cation and anion ternary diagrams. The projections are made along lines that are parallel to Na+K and HCO_3+CO_3 axes. The intersection of the projections represents the composition of the water with respect to six chemical components and is the basis for identifying the hydrochemical facies of a ground-water sample (fig. 18a). Hydrochemical facies are used



Figure 18a--Graphical classification scheme for hydrochemical facies.



Figure 18b--Groundwater from the glacial drift aquifer with less than 450 milligrams per liter dissolved solids (from Wahrer et al., 1992).

to classify the chemical composition of ground water in terms of the dominant cation and anion.

The dominance criteria is based on percentage of milliequivalents of major cations (Ca, Mg, and Na + K) and major anions (Cl, SO₄, and HCO₃ +CO₃) within the ground water. For example, in water dominated by sodium and chloride (Na-Cl facies), the sodium and chloride ions would be greater than 50 percent of the total cations and anions, respectively. A water sample that has no cation or anion that exceeds 50 percent of the total cations facies.

The data used to construct the Piper plot for the glacial drift aquifer consists of 206 water samples with less than 10% charge imbalance. A major limitation in making interpretations from Piper plots is that water samples with very different dissolved-solids concentrations, but with the same relative proportions of cation and anion species will plot at the same position on the diagram. This limitation can be handled in many ways (Hem, 1989). In this thesis this limitation was handled by constructing three Piper plots (fig. 18 b to d) in which the samples are grouped as a function of dissolved solids. The ranges of dissolved solids are less than or equal to 450 mg/L, 451 to 750 mg/L, and greater than or equal to 751 mg/L.

At all ranges of dissolved solids, water samples in the cation ternary diagram plot along a line with very little scatter from the Ca-dominant area to the Na-dominant area. Samples are weighted to Ca dominant at low dissolved solids and Na dominant at high dissolved solids. Water samples in the anion ternary diagram plot between $HCO_3 + CO_3$ and SO_4 dominant solutions at low dissolved solids (fig. 18b), plot among $HCO_3 + CO_3$, Cl and SO_4 dominant solutions at intermediate dissolved solids (fig. 18c) and plot among Cl and SO_4 dominant solutions at high dissolved solids (fig. 18d). The change in the distribution pattern of the data in the diamond area, as a function of increasing dissolved solids, reflects those changes in the cation and anion ternary diagrams.



Figure 18d--Groundwater from the glacial drift aquifer with dissolved solids greater than 751 milligrams per liter (from Wahrer et al., 1992).

The pattern changes in the ternary and diamond diagrams are consistent with a hypothesis in which water masses with various compositions are mixing. At low dissolved-solids concentrations, meteoric water frequently evolves from a Na or Ca - SO₄ dominant rain solution to a Ca - HCO₃ dominant ground-water solution (Berner and Berner, 1987). Such an evolutionary pathway could explain the trends on figure 18b. At high dissolved-solids concentrations, ground water masses that are Na - Cl and Ca - SO₄ dominant are frequently found because of the dissolution of halite (NaCl), gypsum (CaSO₄•2H₂O), and anhydrite (CaSO₄); or the presence of formation brine (Na - Ca - Cl rich solutions). Mixing among such water masses could explain the trends on figure 18d. The trends at intermediate dissolved-solids concentrations (fig. 18c) are most likely the result the mixing of water masses of low (fig. 18b) and high dissolved-solids concentrations (fig. 18d).

A hydrochemical facies map was prepared for the glacial drift aquifer to show the spatial distribution of significant chemical aspects of the facies as classified on the piper plot (figs. 18b to 18d). The hydrochemical facies observed in the glacial drift aquifer are Ca-HCO₃, Na-Cl, Ca-SO₄, and Na-HCO₃ (fig. 19). The predominant hydrochemical facies is Ca-HCO₃ which is consistent with waters that are recently recharged (Back, 1961; Berner and Berner, 1987) (fig. 19). Water from the Saginaw Bay Area is dominantly Na-Cl facies. Ground water in this area also has higher dissolved-solids concentrations than water from other areas. The Na-Cl facies also extends to the south of the Saginaw Bay Area. The Na-Cl facies could be the result of upward advection and diffusion of ions from water from the underlying bedrock aquifers or the dissolution of halite and is consistent with the hypothesis of upwelling of brine from underlying units (Wahrer et al., 1993). Calcium-sulfate facies are found in the northwest portion of the Saginaw Bay Area and extend out toward the west. Water of Ca-SO₄ facies is also found in an area to the southwest of the Saginaw Bay Area. Calcium-sulfate type water is most likely the result of the dissolution of gypsum or anhydrite (Wahrer et al., 1993). Sodium-



Figure 19.-Distribution of Hydrochemical facies in water from the glacial drift aquifer in the lower Peninsula of Michigan (modified from Wahrer et al., 1993).

bicarbonate type water is found just west of the Saginaw Bay Area. The Na-HCO₃ facies is probably the result of mixing between sodium-chloride facies and calcium-bicarbonate facies (Wahrer et al., 1993).

SUMMARY OF GEOCHEMICAL DISTRIBUTION MAPS

Distribution maps based on chemical analyses of ground water from the glacial drift aquifer show general trends that coincide with a regional flow system, suggested by Mandle and Westjohn (1989) that focuses ground-water-flow toward the Saginaw Bay Area and the Michigan Lowland Area.

Most water in the glacial drift aquifer has dissolved-solids concentrations that are less than 1,000 mg/L and dissolved chloride concentrations that are less than 100 mg/L. Dissolved-solids and chloride concentrations increase from the central part of the study area toward the Saginaw Bay Area. Highest measured values were 12,214 mg/L for dissolved solids and 6,714 mg/L for dissolved chloride. Source of solutes for dissolved solids may be from water-rock interaction or through the mixing of meteoric water and formation brine from underlying bedrock aquifers. Source of chloride to the glacial drift aquifer may also be from mixing with formation brine from bedrock aquifers (Long and others, 1988) or from the dissolution of halite probably incorporated in the glacial-drift deposits (Wood, 1969).

Total dissolved iron concentrations for water from the aquifer range from 0.001 to 6.0 mg/L. Iron concentrations less than 0.1 mg/L occur in the northern fringe of the study area and, to a greater extent, in the northwestern part of the study area. Iron concentrations greater than 1 mg/L occur in a large band that extends across the southern part of the study area from the southern part of the Saginaw Bay Area to the Michigan Lowland Area. Most of the southeastern part of the study area has iron concentrations greater than 1 mg/L. Iron concentrations between 0.1 and 1 mg/L occur in ground water

in the eastern and southern fringes of the study area and in the central and north central areas.

Sulfate concentrations in the aquifer range from 1 to 1,800 mg/L. The majority of ground water in the study area has concentrations between 10 and 100 mg/L. In the northern and eastern fringe areas, the northwestern part of the study area, and in a small part of the Saginaw Bay Area, sulfate concentrations are less than 10 mg/L. In the northern and southern parts of the Saginaw Bay Area, there are two large areas where water from the glacial-drift aquifer has sulfate concentrations between 100 and 1,000 mg/L. A small part of the aquifer in the Saginaw Bay Area has water with low sulfate concentrations that could be the result of sulfate reduction. Long and others (1988) have shown that within the Saginaw Bay Area microbial reduction of SO_4^{2-} is occurring.

The distribution of data on Piper plots shows a cation trend from Ca dominant at low dissolved solids to Na dominant at high dissolved solids. The data also show an anion trend from HCO₃+CO₃-SO₄ dominant solutions at low dissolved solids to HCO₃+CO₃-Cl-SO₄ dominant solutions at intermediate dissolved solids to Cl-SO₄ dominant solutions at high dissolved solids. These trends are indicative of a mixing of water masses of various compositions. There are four major hydrochemical facies observed in the Glacialdrift aquifer: Ca-HCO₃, Na-Cl, Ca-SO₄, and Na-HCO₃. The predominant hydrochemical facies is Ca-HCO₃ which is consistent with waters that have recently recharged the aquifer (Back, 1961; Berner and Berner, 1987). Water from the Saginaw Bay Area is dominantly Na-Cl facies and probably the result of upward advection and diffusion of ions from water from the underlying bedrock aquifers or the dissolution of halite. Ground water in this area also has higher dissolved-solids concentrations than water from other areas. Calcium-sulfate facies, which occur in water from the northwest and in an area southwest of the Saginaw Bay Area are most likely the result of the dissolution of gypsum or anhydrite. Sodium-bicarbonate type water is found just west of the Saginaw Bay Area and is probably the result of mixing between sodium-chloride facies and calcium-

bicarbonate facies. The facies distribution also supports the concept of a regional-flow system from the southern and northern uplands of the study area down-gradient to the Saginaw Bay Area.

The water chemistry of the concentrated samples (>1,000 mg/L), which are found in the SLA, were shown to be impacted by physical processes (Long et al., 1988). Although mixing of water masses may be an important process affecting the waters within the SLA, chemical processes must also be considered as significant factors in changing the water chemistry and solute concentrations within the more dilute ground water of the glacial drift aquifer. In the following chapter, the geochemical model WATEQ4F, was used to determine controls on the chemistry of the glacial drift ground water.

Chapter 5

CHEMICAL MODELING

CHEMICAL MODELING

INTRODUCTION

Chemical processes, such as mineral dissolution-precipitation and cation exchange and physical processes, such as ground waters mixing affect differently the relative amounts of dissolved species in ground water (Long et al, 1986). Since water-rock interactions can have a dominant control on the water chemistry of natural waters, geochemical modeling can be a very useful technique. Chemical modeling is used to identify reactive minerals in an aquifer that are controlling the chemistry of ground water by describing the thermodynamic state of solutions (Jenne et al., 1980). Modeling can also be used in the interpretation of the origin and chemical evolution along a flow path. Numerous studies have utilized chemical modeling techniques to further investigate the nature of ground water chemistries or to provide additional information to confirm initial hypotheses.

The source for the concentrated waters of the glacial drift aquifer (dissolved solids > 1,000 mg/L), found in the SLA, have been hypothesized to be from the result of mixing with more concentrated waters from underlying bedrock aquifers. The water chemistry of the dilute water in the glacial drift aquifer (dissolved solids < 750 mg/L) is most likely due to water-rock interactions. Nearly all of the ground water within the glacial drift aquifer is affected to some degree by chemical processes. In order to determine which mineral components in the aquifer are reacting with the ground water and affecting the water chemistry, the water from the glacial drift aquifer was chemically modeled using the computer code WATEQ4F (Ball et al, 1991).

Field measurements of temperature, pH, pe, dissolved oxygen, alkalinity, dissolved species concentrations, and calculated density is used for each sample. From this data, WATEQ4F is able to calculate the elemental speciation, activities and activity coefficients of the dissolved species, and mineral saturation indices that indicate the tendency of water

to precipitate or dissolve a set of minerals (Ball et al., 1991). The SI of a mineral is defined by the equation:

$$SI = \log \frac{IAP}{K_{T}}$$
(8)

where IAP is the ion activity product of the mineral water reaction and K_t is the thermodynamic equilibrium constant adjusted to the temperature of the sample. If the SI is equal to or approximately equal to zero, the water is at equilibrium with a specific mineral phase. When the SI is positive, the water is supersaturated with respect to that mineral phase, and the mineral would tend to precipitate from solution. When the SI is negative, the water is undersaturated with respect to the mineral phase, and the mineral with respect to the mineral phase, and the mineral with respect to the mineral phase, and the mineral with respect to the mineral phase.

The success of chemical modeling depends on the quality of data and an accurate and internally consistent database. Therefore, data with only less than ten percent difference in charge balance were modeled and the most complete thermodynamic data set available for solubility product constants and ion association constants was used. Equilibrium constants and enthalpy values used in the modeling for the minerals discussed in this chapter are included in table 2. Three mineral systems were investigated with the use of WATEQ4F; the carbonate minerals (aragonite, magnesite, dolomite, and calcite), the evaporite minerals (anhydrite, gypsum, halite), and the silicate and alumino-silicate minerals (chalcedony, cristobalite, talc, quartz). Frequency histograms of selected mineral saturation indices, as well a mineral stability diagram (activity-activity), are used to evaluate and interpret the chemical modeling data. Distribution maps (iso-equilibrium) of the mineral saturation indices have been created but no regional trends are present. Therefore, the maps are not included in this thesis. The minerals investigated were selected because they are representative of the mineralogy of the glacial drift deposits.

-1.71 -2.589 -2.297 -11.09 -0.109 0.918 35.3	<u>log K</u> -4.36 -8.336 -8.480 -16.54 -4.58 1.582 7.434 25.34	<u>Keterences</u> Langmuir and Melchior, 1985 Plummer and Busenberg, 1982 Plummer and Busenberg, 1982 Wagman et al., 1982 Langmuir and Melchior, 1985 WATEQ2; Ball et al., 1980 ΔH from Robie et al., 1979 log k from May et al., 1976 Baes and Mesmer, 1976
5.99	-3.98	Fournier, 1985

Table 2 Thermodynamic equilibrium constants and enthalpy values
Density of each water sample was used as input to the model. The density of water varies with temperature and salinity and therefore, it is possible to calculate the density of a water sample by using a series of equations described by Gudramovics (1981). At a constant temperature, the relationship between density and salinity is linear, as shown by the following equation:

density =
$$(salinity * slope) + y$$
 intercept (9)

To determine the density one must first determine the salinity. The salinity was estimated from the chloride concentration using the following equation by Schopf (1980):

$$salinity = 1.80655 * (Cl)$$
 (10)

To calculate the density of water at the measured temperature in the well, the value of the y-intercept and slope must be calculated. The y-intercept refers to the density of pure water at a specified temperature and is determined through the following equation by Weast (1979):

y-intercept =
$$(999.83952 + 16.945176 * T - 7.9870401 * 10^{-3} T^{2} - 46.170461 * 10^{-6} T^{3} + 105.56302 * 10^{-9} T^{4} - 280.54253 * 10^{-12} T^{5})/(1 + 16.87985 * 10^{-3} * T) * 1000$$
(11)

The slope for the specified temperature is calculated from the equation by Horne (1969):

slope = $8.300245 * 10^{-4} - 2.2274915 * 10^{-5} * \ln T$ (12)

After the salinity, y-intercept and slope are calculated at the temperature of the sample, the density can be calculated using equation (9).

SATURATION INDICES

Carbonate Minerals

The carbonate minerals investigated include aragonite, magnesite, dolomite, and calcite. Most of the SI data, for the mineral aragonite, range from approximately -0.5 to 0.7, with an average value of -0.0024 (fig. 20). This data suggests the water is in



Figure 20-Frequency histograms of saturation index values for aragonite and magnesite from water in the glacial drift aquifer.

equilibrium with respect to the mineral aragonite. There are no regional trends observed on the iso-equilibrium map for aragonite. The SI data for the mineral magnesite generally range from -1.3 to -0.1, with an average value of -0.7263 which indicates the water is slightly undersaturated with respect to magnesite (fig. 20). The iso-equilibrium map for magnesite indicates that SI values are generally less than -0.8 throughout the aquifer and values greater than -0.9 are found locally in areas of the SLA and in the north part of the aquifer. Modeling results for the mineral dolomite indicate most of the data falls between -1.8 and 0.9 with an average value of -0.6556. This suggests the water is slightly undersaturated with respect to dolomite in the glacial drift aquifer (fig. 21). The isoequilibrium map for dolomite indicates a few scattered localized areas in the glacial drift aquifer where water is saturated with respect to dolomite. SI data for the mineral calcite indicate a range of -0.4 to 0.8 with an average value of 0.1523, which indicates the water is in equilibrium or just slightly over saturated with respect to calcite (fig. 21). The isoequilibrium map for calcite indicates that most of the water in the aquifer is just slightly oversaturated and only a few scattered localized areas have water that is undersaturated with respect to calcite.

Evaporite Minerals

The evaporite minerals investigated from the glacial drift aquifer include anhydrite, gypsum and halite. The modeling results suggest that most of the SI data for the mineral anhydrite fall between -3.4 and -0.6 with an average value of -2.300 (fig. 22). This data suggests the water from the glacial drift aquifer is undersaturated with respect to the mineral phase anhydrite. There is no regional trend observed on the iso-equilibrium map for anhydrite. Most of the SI data for the mineral gypsum range from -3.4 to -0.8 with an average value of -2.0465 and indicates the water is also undersaturated with respect to gypsum (fig. 22). The iso-equilibrium map for gypsum indicates no observable regional trend. Results for the mineral halite indicate a range from -3.4 to -10.25, which suggests



Figure 21-Frequency histograms of saturation index values for dolomite and calcite from water in the glacial drift aquifer.



Figure 22--Frequency histograms of saturation index values for anhydrite, gypsum, and halite from water in the glacial drift aquifer.

the water in the aquifer is undersaturated with respect to the mineral phase halite (fig. 22). The iso-equilibrium map for halite indicates no significant regional trends.

Silicate Minerals

The silicate minerals investigated from the glacial drift aquifer include chalcedony, cristobolite, talc, and quartz and were selected because they are closest to equilibrium. Modeling results for the mineral chalcedony indicate most of the SI data range from -0.4 to 0.25 with an average value of -0.0195 (fig. 23). This suggests the water is in equilibrium with respect to chalcedony. The iso-equilibrium map for chalcedony indicates no regional trends throughout the aquifer. Most of the SI data for the mineral cristobalite range from -0.4 to 0.3 with an average value of 0.0421 which suggests the water is in equilibrium with respect to cristobalite (fig. 23). The iso-equilibrium map for cristobalite also shows no regional trends. The modeling results for the mineral talc indicate the SI data range from -5.0 to 3.0 with an average value of -2.0132 which indicates the water is undersaturated with respect to talc (fig. 24). The iso-equilibrium map for talc indicates there are scattered localized areas where talc is oversaturated with respect to the mineral phase talc. SI data for the mineral quartz indicate that most data range from 0.0 to 0.7, with an average value of 0.4552 (fig. 24). This distribution suggests the water is near equilibrium to slightly oversaturated with respect to quartz. The iso-equilibrium map for quartz indicates that there are no regional trends within the aquifer.

ALUMINO-SILICATE MINERALS

Due to the difficulty in determining the controls on the solubility of Al, the stability relationships of alumino-silicate minerals are commonly studied by utilizing activityactivity diagrams (Hull, 1984; Henderson, 1985; Drever, 1988). These diagrams are based on the activities calculated from chemical modeling and on the thermodynamic stability fields. This graphical technique uses the assumption that all of the Al in the system is



Figure 23-Frequency histograms of saturation index values for chalcedony and cristobalite from water in the glacial drift aquifer.



Figure 24—Frequency histograms of saturation index values for talc and quartz from water in the glacial drift aquifer.

retained in the solid phases. On the basis of this assumption, the stability fields of Al bearing minerals can be described in terms of the activities of the other dissolved species of the rock-water system.

In figure 25, the data from the glacial drift aquifer are plotted onto the activityactivity diagram for the K-Al-Si system. The mineral stability fields presented on figure 25 are based on Velbel (1992). The placement and extent of the illite stability field is based on an idealized illite-surrogate as defined by Grim (1968). Most of the glacial-drift ground water data plot within the illite and kaolinite stability fields, straddling the illite/kaolinite stability field boundary. This indicates that most of the glacial-drift ground water have the potential to be in thermodynamic equilibrium with respect to illite and kaolinite. These minerals have been shown to be present in the glacial-drift deposits in the SLA (Chittrayanont, 1978).

SUMMARY OF GEOCHEMICAL MODELING

Chemical modeling results indicate that water-rock interaction is impacting the solute concentrations of water from the glacial drift aquifer. The ground water in most of the study area may be attributed to varying amounts of carbonate and evaporite mineral dissolution. The ground water was also shown to have the potential to be in thermodynamic equilibrium with the clay minerals illite and kaolinite. Clay minerals such as chlorites and smectites may also affect water chemistry, but to what degree is uncertain. The solutes in the dilute water of the aquifer (dissolved solids < 750 mg/L) are believed to be controlled dominantly by water-rock interaction. It has been hypothesized that a significant amount of water-rock interaction takes place in the glacial drift aquifer prior to water entering the Grand River-Saginaw or underlying aquifers (Wahrer et al., 1993; Meissner, et al., 1993). Nearly all the water entering the study area must initially go through the glacial-drift deposits and reacts with the various mineral constituents and becomes less reactive or in equilibrium with certain minerals before entering the



Figure 25-Mineral stability diagram for the potassium alumino-silicate minerals. The stability fields are based on Velbel (1992).

underlying aquifers. The SI results from modeling waters in the Marshall aquifer (Meissner, et al., 1993) and the Grand River-Saginaw aquifer (Wahrer et al., 1993;) indicates very similar results with the SI data from the glacial drift aquifer.

Although water-rock interaction is the dominant control on the solutes of the dilute ground waters in the glacial drift aquifer these processes cannot explain the distribution of all constituents, especially in the more concentrated waters of the SLA. A physical process, such as mixing, could be affecting the distribution of species that aren't related to any of the above chemical dissolution-precipitation processes. In the following chapter, Cl/Br ratios and log-log diagrams are used to investigate the extent water-rock interactions, as well as physical processes, may have had on the water chemistry of the glacial drift aquifer.

Chapter 6

GEOCHEMICAL DATA REDUCTION AND RESULTS

GEOCHEMICAL DATA REDUCTION AND RESULTS

INTRODUCTION

In order to study the chemical evolution of the water, it is necessary to separate the water samples into two phases; the solute and the solvent. The solute is the dissolved chemical species within the ground water sample, whereas the solvent is the water molecule itself. The chemical data will be used in this chapter to determine the source of the solutes for the water in the glacial drift aquifer. The isotope data will be used in determining the source and relative age of the water molecule and is discussed in chapter 7.

The solute concentrations in the ground water of the glacial drift aquifer may be influenced by both water-rock interactions and interaction with more concentrated waters from underlying aquifers. In chapter 5, the chemistry of the glacial drift ground water was shown to be greatly impacted by water-rock interactions. However, the ground water that is found in the SLA has dissolved-solids concentrations greater than 1,000 mg/L (fig. 14) which indicates the source of the dissolved constituents in this area are influenced by processes other than water-rock interactions. Brine is known to exist in bedrock aquifers below the glacial drift and could be a source for high solutes in water sampled from the SLA.

ANALYSIS OF CI/Br RATIOS

To investigate the source of chloride in the SLA, Cl/Br ratios are a useful analysis. Brine from the Michigan basin are known to contain up to a few thousand parts per million of bromide (Wilson and Long, 1986) while halite contains concentrations of only trace amounts to several hundred parts per million of bromide (Holser, 1979). A study performed by Wilson and Long (1984), showed that by dissolving halite, that contained 150 ppm bromide, a Cl/Br ratio of 3025 would result. Therefore, in comparing Cl/Br ratios, a solution that is formed by dissolving halite would have a Cl/Br ratio of at least

3025, whereas oil field brines from the Michigan basin would have Cl/Br ratios ranging from 400 to 600 (Wilson and Long, 1984).

Figure 26 is a frequency histogram of Cl/Br data from the glacial drift aquifer, with values ranging from 13.3 to 2545.4 mg/L. The Cl/Br ratios correspond with brine ratios from the Michigan basin rather than with ratios from halite dissolution. Data that plot significantly to the left of the brine area are fresh water. Several data plot to the right of the brine ratio (fig. 26) which implies that they may be related to the dissolution of halite from salt that is heterogeneously distributed in the glacial-drift deposits (Wood, 1969) or from road salt.

LOG LOG DIAGRAMS

The frequency histogram (fig. 26) indicates that the major source of the high chloride concentrations in the glacial drift aquifer can be linked to brine in the underlying aquifers. Mixing between brine and less concentrated waters in the Michigan basin may be one explanation for the source of concentrated waters found in both the Pennsylvanian sequence (Meissner, 1993) and the glacial drift aquifer. Carpenter (1978) demonstrated that formation water chemistry can be compared with evaporating sea water to make interpretations on the origin and evolution of water chemistry.

During the evapo-concentration of sea water, the ratios of ions in solution remain constant until mineral precipitation begins. This constant relationship between ions can be expressed in a logarithmic equation of the form:

$$\log B = \log A + \log k \tag{13}$$

where A and B are ions and k is a constant. A log-log plot of this data would produce a straight line with a 1:1 slope and any ion that deviates from this relationship would be affected by some process other than the removal of water (Carpenter, 1978). To demonstrate this relationship one or more conservative constituents are required. Bromide and chloride were selected because during the initial evaporation of sea water,



Figure 26-Frequency histogram of Cl/Br ratios for water from the glacial drift aquifer. Also shown are ranges for brine and halite Cl/Br ratios.

both chloride and bromide behave conservatively (Carpenter, 1978; McCaffrey et al., 1987). Bromide is the preferred constituent and is used in figures 27 and 28. However, due to the lack of bromide data in the more concentrated samples, Cl was used as a conservative indicator in figures 29 through 33. These plots are used to indicate any effects of water-rock interaction, mixing or any similarities between the waters of the glacial drift aquifer and the underlying Grand River-Saginaw, Parma Bayport, and Marshall aquifers.

Figure 27 shows the relation between chloride and bromide. Previous work has shown that data from the near-surface bedrock aquifers (Meissner, 1993) have a similar distribution as the data from the glacial drift aquifer. The distribution of data from the glacial drift aquifer displays a scattering of dilute waters with the more concentrated samples focusing toward the seawater evaporation trajectory. The more dilute waters extend back from the concentrated waters which indicates a dilution effect. The scatter associated with the dilute waters indicates there is a freshwater endmember with variable Cl and Br concentrations. This freshwater endmember appears to be affected by other sources of solutes and less affected by mixing with very concentrated waters. The very dilute waters tend to curve downward and appear to hit a vertical boundary; which is probably due to added sources of Br (Wilson, personal communication, 1993).

Figure 28 shows the relation between sodium and bromide while figure 29 shows the relation between sodium and chloride. As in figure 27, a dilute end-member water exists and is relatively unaffected by the very concentrated waters (brine). However, as the concentration of the glacial drift samples increases, they tend to focus toward the composition of seawater. The data on the diagrams also indicate there is an increasing degree of concentration among the aquifers, with the glacial drift aquifer having the least degree of concentration and the Marshall aquifer the most. Concentrated water from the Parma Bayport brine and Marshall brine samples plot beyond seawater composition and follow the seawater evaporation trajectory that suggests they were formed through the



Figure 27-Plot showing the relationship between log Cl and log Br from water in the glacial drift aquifer.



Figure 28-Plots showing the relationship between log Na and Log Br from water in the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers.



form water in the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers.

evapo-concentration of seawater. These plots also provide evidence for a downward mixing trend or dilution trend from past seawater composition back towards less concentrated waters.

Figure 30 shows the relation between calcium and chloride. The distribution of data from the glacial drift aquifer indicates that nearly all water samples are enriched in calcium with respect to the seawater evaporation curve. The data also suggests a dilution trend exists that extends slightly downward and to the left away from the composition of seawater. Looking at the distribution of data from all the aquifers reveals that the dilution trend extends from an area beyond seawater composition, back to less concentrated waters. The dilute waters tend to cluster in an area with a constant calcium concentration that may suggest the waters are not directly related to the deep concentrated waters of the basin, but are controlled through water-rock interaction.

Figure 31 shows the relation between magnesium and chloride. Data from the glacial drift aquifer tends to have a similar distribution as the less concentrated waters of the bedrock aquifers. The more dilute glacial drift waters probably have many sources of solutes through the processes of water-rock interaction. The more concentrated samples of the aquifers are depleted in magnesium relative to the seawater evaporation curve. A possible mechanism that would elevate calcium and deplete magnesium concentrations is dolomitization of limestone (Carpenter, 1978). Wilson (1989) in a study of Devonian and Silurian formations brines of the Michigan basin found dolomitization to be a major diagenetic reaction controlling calcium and magnesium concentrations. Data on (figs. 29-31) indicate that only the more concentrated waters from the glacial drift aquifer are effected or related to the underlying formation brines.

Figure 32 shows the relation between potassium and chloride. Data distribution from the glacial drift aquifer shows a similar pattern to the data distributions from the bedrock aquifers. The more concentrated samples of the Marshall aquifer are depleted in potassium and trend parallel to and beyond the concentration of seawater.



Figure 30-Plots showing the relationship between log Ca and log Cl from water in the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers.



Figure 31-Plots showing the relationship between log Mg and log Cl from water in the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers.



Figure 32-Plots showing the relationship between log K and log Cl from water in the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers.

Figure 33 shows the relation between sulfate and chloride. Data from the glacial drift aquifer show a very scattered distribution, although there is a small cluster of data. The scattered distribution of data suggests that there may be several sources of sulfate which could include sulfate dissolution and sulfate reduction. Long and others (1988) have shown that sulfate reduction is a process occurring in Bay County, Michigan. In the other three aquifers the most concentrated samples tend to be depleted in sulfate with respect to the seawater evaporation curve. Wilson (1991), noted that sulfate reduction was a process causing depletion of sulfate in Devonian and Silurian brines. This same process could produce the distribution of data that is seen for the Parma-Bayport and Marshall aquifers (Meissner, 1993; Bauer, 1993).

An interesting distribution to note is that there is a gap in the Marshall data that is bridged by the concentrated Parma-Bayport samples (fig. 33). This distribution suggests that the most concentrated waters of the Marshall brine that are depleted in sulfate are probably isolated from the overlying bedrock and glacial drift aquifers. This would suggest that the source of solutes to the glacial drift aquifer is brine in the Parma-Bayport aquifer or concentrated waters from the Grand River-Saginaw aquifer.

SUMMARY OF RESULTS

The frequency histogram of Cl/Br ratios from the glacial drift aquifer (fig. 26) indicate that the major source of Cl to the aquifer is most likely a brine than from the dissolution of halite. The data distribution from the ion:Cl and ion:Br diagrams (figs. 27 - 33) indicate that the most concentrated waters from all of the aquifers have a very similar distribution and the source of solutes may be related. These diagrams also indicate that there are two end member waters; a saline end member, and a dilute end member, as well as mixed waters. Mixing between these two end member waters could explain the distribution of high solutes observed in the glacial drift aquifer. The location of the high



Figure 33-Plots showing the relationship between log SO4 and log Cl from water in the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers.

concentrated waters of the glacial drift aquifer is in and around the SLA, while in general the remainder of the study area has dilute ground water (fig. 14).

The chloride-rich end-member water is shown to be impacting the water chemistry of a portion of the glacial drift aquifer as indicated by the dilution trend or mixing trend back from very concentrated waters of the Parma-Bayport and Marshall aquifers (figs. 28 - 33). The distribution from the ion:Cl diagrams (figs. 28 - 33) indicates that the high concentrated solutes in the glacial drift aquifer and the near-surface-bedrock aquifers are similar and that the fluid was concentrated to past halite precipitation and had been enriched in calcium and depleted in magnesium, potassium, and sulfate with respect to the seawater evaporation curve.

The dilute end member waters of the glacial drift aquifer generally plot as a scattered distribution (figs. 27 -33) that suggests these waters are probably isolated from the interaction with the brine or concentrated waters of the underlying aquifers. This distribution also indicates that the ground water has several sources of solutes. The source for most of these solutes is probably derived from water-rock interactions that take place in the glacial drift. The glacial-drift deposits consist of a wide range of minerals that could contribute to the dissolved-solids concentrations. This interpretation is also supported by the results of the chemical modeling which indicated that a major source of the solutes to the dilute ground waters was probably derived from water-rock interactions.

Anthropogenic processes could also have caused some of the high dissolved solids in the SLA or just enhanced a natural process that was already occurring (Takacs and others, 1988). Fractures would allow the solutes to reach the overlying units more easily. The ion:Cl diagrams (figs. 28 - 33) also indicate that brine from the Pennsylvanian and Mississippian aquifers are chemically similar which makes it difficult to decern which brine may be affecting ground water in the glacial drift aquifer. It seems more reasonable therefore, that the brine in the Parma-Bayport is the original source for the majority of the high concentrated waters found in the glacial drift aquifer (fig. 33). However this brine

would have first interacted with water from the Grand River-Saginaw aquifer which in turn would have impacted the ground water in the glacial drift aquifer. The interaction between infiltrating meteoric water into the glacial drift aquifer and mixing with the concentrated water of the Grand River-Saginaw and Parma-Bayport aquifers could produce the water chemistry that is present.

Chapter 7

ISOTOPE DATA REDUCTION AND INTERPRETATION

ISOTOPE DATA REDUCTION AND INTERPRETATION

INTRODUCTION

The differences in mass of the isotopes cause isotope fractionation (Drever, 1988). Fractionation is any process that causes the isotopic ratios in particular phases or regions to differ from one another (Drever, 1988) and can be caused by either a chemical or physical process. Isotopic analyses are very important in geochemical studies and become even more valuable when the interpretations are combined with the results from graphical, hydrogeological, statistical and geochemical modeling analyses.

The stable isotopic ratios of oxygen, hydrogen, carbon, and sulfur were measured in selected ground water samples from the glacial drift aquifer in order to investigate the source and relative age of the water molecule in ground water. $\delta^{18}O$ and δD interpretations are based on sections from Wahrer et al., 1993. Different $\delta^{18}O$ and δD compositions can be used to identify ground-water masses, mixing trends between water masses, and age (Gat, 1981; Fontes, 1981; Frape and others, 1984; Long and others, 1986 and 1988). The $\delta^{13}C$ and $\delta^{34}S$ can be used to determine the sources of carbon and sulfur in the ground water, chemical controls on the evolution of a water mass, and the identification of microbiological processes (Hartmann and Nielson, 1969; Rightmire and Hanshaw, 1973; Rightmire and others, 1974; Thorstenson and others, 1979; Anderson and Arthur, 1983; Kaplan, 1983; Long and others, 1986 and 1988).

The isotope composition of oxygen and hydrogen is reported in terms of the difference of the ${}^{18}O/{}^{16}O$ and $D/{}^{1}H$ ratios relative to SMOW (Standard Mean Ocean Water). The isotope ratios are reported as $\delta^{18}O$ and δD values where the ratio is expressed as parts per thousand or parts per mil deviations from that of SMOW. The ratio of ${}^{13}C/{}^{12}C$ is reported as $\delta^{13}C$. The standard for $\delta^{13}C$ is the carbonate belemnite from the Pee Dee Formation of South Carolina (PDB). SMOW is also another commonly used standard for carbon and has a $\delta^{13}C$ value of -30.86 ‰ on the PDB scale. The ratio

of ³⁴S to ³²S is the most frequently studied of the sulfur isotopes and is expressed in terms of δ^{34} S. The standard for δ^{34} S is the S in troilite (FeS) of the iron meteorite Canyon Diablo (collected at Meteor Crater, Arizona), whose ³²S/³⁴S ratio is 22.22.

The δ values can be calculated by using the following formula:

$$\delta = \frac{\left[R_{x} - R_{std}\right]}{R_{std}} \times 10^{3}$$
(14)

where R_x is the isotopic ratio in the sample and R_{std} is the isotopic ratio in the standard (Faure, 1986). Because the differences between the standard and the sample are often small, the ratio is multiplied by 1,000. Waters with negative δ values are enriched in the lighter isotope compared to standard and waters with positive δ values are enriched in the heavier isotope compared to standard.

OXYGEN AND HYDROGEN ISOTOPES

δ^{18} O and δ D comparison

Figure 34 is of δD versus $\delta^{18}O$ for 194 ground-water samples collected from the glacial drift aquifer. These data are compared to the global-meteoric water line of Craig (1961) and the Simcoe Line, a local-meteoric water line developed for Simcoe, Ontario, Canada (Desauliniers and others, 1981). The Simcoe data were collected from precipitation approximately 120 miles east of the study area. The equation for the Craig line is $\delta D = 8*\delta^{18}O + 10$ and the Simcoe line is $\delta D = 7.5*\delta^{18}O + 12.6$. The data distribution from the glacial drift aquifer coincides with trends of the Simcoe and global meteoric water lines and is interpreted to indicate the water is of meteoric origin.

A wide range of isotopic signatures of meteoric water exist in the glacial drift aquifer. Heaviest δ^{18} O values range up to -8.0 ‰ and are interpreted to indicate recent meteoric water. Isotopic signatures as light as -18.8 ‰ are found within the glacial drift aquifer and have been interpreted to indicate that some water must have recharged the



Figure 34.—Plot showing the relationship between δD and $\delta 180$ for water from the glacial drift aquifer. The composition of oxygen and hydrogen is reported in terms of the difference of the 180/160 and D/1H ratios relative to Standard Mean Ocean Water (SMOW). The δD and $\delta 180$ values of SMOW are zero.

aquifer at a time when the climate was much cooler, such as during the most recent glaciation (Long and others, 1988; Wahrer et al., 1993). From the distribution of data on figure 34, two distinct water masses are present; modern meteoric water and glacial-age meteoric water. A mixture of modern meteoric water and glacial-age meteoric water have mixed to cause a continuum of plotted values.

Distribution Map

The δ^{18} O and δ D values for most ground water samples from the glacial drift aquifer range from -12.4 to -8.3 % and from -83.5 to -56.0 %, respectively (fig. 34). However, parts of the Saginaw Bay Area have values of δ^{18} O from -18.8 to -11.0 ‰ and values of δD from -137.4 to -75.0 ‰. The mean $\delta^{18}O$ and δD values are -11.2 and -76.1 3. The same spatial trends are generally observed for both δD and δ^{18} O and, therefore, a map of the spatial distribution of δD has not been included. Figure 35 shows the spatial distribution of δ^{18} O values for the glacial drift aguifer. Two regional trends are observed from the distribution of the δ^{18} O values. The first is a north-south trend in which the δ ¹⁸O values become lighter from the southern part of the study area northward. Values of δ^{18} O in the south range from -8.7 to -10.6 ‰, and in the north range from -10.0 to -12.4 %. These data do not reflect seasonal isotopic variability in recharge water because ground water typically homogenizes this variability into a yearly average (Lloyd and Heathcote, 1985; Long and others, 1988). However, the yearly average isotopic signature of recharge water is probably not the same throughout the basin (Gat and Gonfiantini, 1981). For example, Sheppard and others (1969) contoured δD and $\delta^{18}O$ values in recent precipitation for North America. Their data show that δD and $\delta^{18}O$ become lighter in the precipitation from south to north latitude. In Michigan, a south to north gradient of δD values from -50 to -60 ‰ and $\delta^{18}O$ values from -7.5 to -10 ‰ was shown.

The δ^{18} O values presented by Sheppard and others (1969) are slightly heavier than those of the north-south gradient found in water from the glacial drift aquifer for this



Figure 35.-Variation of δ 18O in water from the glacial drift aquifer in the lower Peninsula of Michigan (from Wahrer et al., 1993).

study. This variation in δ^{18} O values can be explained by the fact that, in Michigan, ground-water recharge may be greater in the cool months of late fall and early spring (Vanlier, 1963) rather than mid-summer. Precipitation during colder temperatures is more depleted in ¹⁸O and D than during warmer temperatures (Gat, 1980). Increasing the weighting of these months in the calculation of the yearly average isotopic signature for a latitude would tend to "lighten" the mean compared to the values presented by Sheppard and others (1969) as shown by (Long and others, 1988).

The glacial drift aquifer also has some of the lightest δ^{18} O values (-18.8 ‰) within the basin. These very light signatures are found in the Saginaw Lowland Area and are significantly lighter than expected from modern recharge (fig. 35). Regalbuto (1987) found recent ground water from glacial-drift deposits on the Leelenau Peninsula, which is north of the Saginaw Lowland Area, to have δ^{18} O values that range only between -11.81 and -13.03 per mil. Thus, the very light values found in the Saginaw Lowland Area are anomalous and are interpreted to indicate that ground water recharged the system when the climate was cooler (Long et al, 1988). This interpretation is consistent with findings of other investigators who have discovered very light δ^{18} O and δ D values in ground water in areas similar to the Michigan basin (Perry et al., 1982; Fritz et al., 1974; Desauliniers et al., 1981 and Siegel and Mandle, 1984).

The trend of the δ^{18} O signatures in the SLA shows values ranging from -11.0 to -18.8 ‰ (fig. 35) decreasing towards Saginaw Bay. A similar distribution of δ^{18} O values, in part of the Saginaw Bay Area, also occurs in water from Pennsylvanian bedrock aquifers beneath the drift (Meissner, 1993). The isotopically light water in the Saginaw Bay Area retains its isotopic signature due to slow flushing of the system by present-day recharge water. The slow flushing appears to be due to the presence of relatively impermeable sediments mapped as glaciolacustrine clay. (Long and others, 1988; Mandle and Westjohn, 1989).

<u>Cl versus $\delta^{18}O$ </u>

Figure 36 is a plot of δ^{18} O versus Cl which can be used to determine if there is a relationship between the glacial age water (isotopically light) and the concentrated waters that are providing the high solutes to the area. The distribution of data on the δ^{18} O versus δ D plot (fig. 34) indicates mixing of water masses. The waters that are isotopically light and have high dissolved solids (eg. high chloride concentrations) are located in the same areas of the aquifer (figs. 14, 15, 35). The observed trend on figure 36 shows that as the chloride concentrations increase to approximately 100 mg/L, the δ^{18} O values stay relatively the same. However, as the chloride concentrations increase to >100 mg/L, the δ^{18} O signature of the corresponding sample becomes much lighter. There are a few exceptions where very light isotopic signatures are associated with samples that are very dilute (fig. 36). The pattern is unclear in this context.

Discussion of δ^{18} O and Cl distribution

To better investigate this pattern it is necessary to put it into the context of the whole basin. A study by Long et al (1993) used δ^{18} O and chloride data from the glacial drift, Grand River-Saginaw, Parma-Bayport, and Marshall aquifers, as well as from Clayton et al (1969). From this study Long et al (1993) were able to define a mixing relationship between waters in the Michigan basin. The mixing relationship was based on the idea that only a small amount of chloride from a brine would be needed to produce the observed chloride concentrations in the mixed waters and would therefore, not effect the isotopic signature to any great degree.

To investigate this hypothesis a brine and a freshwater end member were mixed in various proportions and the resultant δ^{18} O values and chloride concentrations were calculated. The freshwater end member was assigned a chloride concentrations of 1.0 mg/L and δ^{18} O values were assigned to represent the isotopic signature of "heavy" recent meteoric water (-8.0), average recent meteoric water (-10.0), and isotopically light


"glacial" age meteoric water (-20.0) from within the basin. The brine end member was assigned a chloride concentration of 200,000 mg/L and a δ^{18} O value of 0.0 permil, based on data from Clayton et al (1966). The chloride concentrations were calculated by weight-averaging the end members and the δ^{18} O values of the mixed waters were calculated using the equations:

$$\delta^{18}O_{\text{mixture}} = F * X * \delta^{18}O_{\text{brine}} + (X-1) * \delta^{18}O_{\text{fresh}}$$
(15)

$$Cl_{mixture} = X * Cl_{brine} + (X-1) * Cl_{meteoric}$$
 (16)

where F is the ratio of the H_2O weight in brine to its weight in pure water and X is the fraction of brine mixed. A value of 0.70 was used for F in these calculations (Wilson and Long, 1993).

The results observed on figure 37 indicate that all the data fall within the mixing envelope defined by the -8.0 and -20.0 permil δ^{18} O values. The δ^{18} O values of the mixtures remain relatively constant over a large concentration range. The δ^{18} O values do not change significantly in the mixture until chloride concentrations reach 10,000 mg/L, which would be freshwater mixed with 5% brine. With these results, Long et al (1993) showed that mixing of freshwater (recent and "glacial" meteoric) with various amounts of brine can account for the chloride concentration and δ^{18} O signatures of ground water found in the study area. Therefore, it is hypothesized that mixing of concentrated waters from below the glacial drift aquifer with glacial meteoric and modern meteoric waters is providing the high solutes observed in the glacial drift aquifer without impacting the isotopic signatures of the glacial meteoric water.

There are several interpretations that are concluded from the analysis of the isotope and Cl data (figs. 34 - 37). First, the isotopically light water in system is there because of slow flushing of the system by present-day recharge water. Secondly, the combination of the SLA being a regional discharge area and the presence of fine-grained



till provide slow moving water and salt to this area. And finally, the glacial activity (isotopically light water) and the introduction of impermeable material (clays) have greatly affected the SLA ground water.

CARBON ISOTOPES

The isotopes in the carbon reservoirs may be thought of as being "heavy" (+2 to -2) for carbonate minerals, "medium" (-5 to -7) for atmospheric CO₂, and "light" (-20 to -30) for organic matter and soil CO₂ (Long et al, 1986). These differences in δ^{13} C are the basis of being able to differentiate sources of carbon in an aquifer. The δ^{13} C value of a ground water is determined by the δ^{13} C of the inflow water and the supply of carbon to and removal of carbon from, water during its movement within the aquifer (Drever, 1988). It is important to note that dissolved organic carbon is likely to be the result of many carbon sources (Long et al, 1986). Coal and black shales, microbiological production of CO₂, and carbonate minerals are several possible sources of carbon that are investigated.

Ninety-four ground water samples from the glacial drift aquifer were measured for their ${}^{13}C/{}^{12}C$ isotope ratios. The ground waters have $\delta^{13}C$ values ranging from -19.0 to -7.0 ‰ with an average value of -13.2 ‰ (fig. 38). The majority of data fall between - 11.0 to -16.0 ‰. In the Bay county area, Long et al (1988) indicated that organic material was a more important source for carbon than carbon derived from carbonate minerals. A $\delta^{13}C$ value of -15.0 ‰ is the lower limit expected for a mixed carbonate mineral-organic source (Long et al, 1986). The possible sources of organic carbon in the aquifer include organics associated with coal and black shales, buried soil horizons, and anthropogenically derived wastes. There may also be a combined influence from organic matter and from carbonate minerals such as calcite, aragonite, and dolomite that are found in the drift. A combined source of carbon consisting of lignitic material (-25.0 ‰) and carbonate minerals (0.0 ‰) result in an average value for $\delta^{13}C$ in ground water of -12.1



Figure 38-Frequency histogram of δ 13C from water in the glacial drift aquifer. Also shown are the ranges for δ 13C in various natural systems.

% (Thorstenson and Others, 1979). This is consistent with a large number of the glacial drift δ^{13} C values.

SULFUR ISOTOPES

Sulfate may be derived in ground water from the dissolution of calcium-sulfates and through the oxidation of iron-sulfides. In this thesis, the reaction of interest is the microbiological reduction of sulfate to sulfide:

$$2 H + SO_4 + 2[CH_2O] = 2 H_2O + H_2S + 2CO_2$$
(17)

From the process of sulfate reduction, sulfate concentrations are depleted and δ^{34} S is enriched. The fractionation of sulfur isotopes occurs during the reduction of sulfate by bacteria and through isotope exchange reactions among S-bearing ions and molecules in aqueous solutions (Faure, 1991). The fractionation of sulfur isotopes appears to be due to bond strength with ³⁴S forming stronger bonds than ³²S (Long et al., 1986). The bacteria identified to be of primary importance in the reduction of sulfate is Desulfovibrio and Desulfatomaculum (Long et al, 1986). These anaerobic bacteria are able to flourish by oxidizing organic matter using oxygen derived from sulfate ions. Through this process, they reduce sulfur and excrete it as H₂S, which is enriched in ³²S compared to the sulfur (Faure, 1991).

In a 1986 study on ground water in Bay County, Michigan, Long and others used sulfur and carbon isotopes to determine sources of sulfate to the ground water samples. Their study focused on the ground water from the glacial drift and Grand River-Saginaw aquifers and concluded that sulfate reduction was occurring in the Bay County ground waters.

Twenty-two ground water samples were measured for $\delta^{34}S$ (fig. 39). Data used is from RASA (Dannemiller and Baltusis, 1990) (15 samples) and from Long et al, 1986 (7 samples). The distribution of data shows that the heaviest $\delta^{34}S$ values are found in the SLA. Figure 40 is a frequency histogram of the $\delta^{34}S$ values in dissolved sulfate from the



Figure 39.—Map showing the distribution of δ 34S in water from the glacial drift aquifer.

glacial drift aquifer. The values range from -2.1 to 52.73 ‰ and have an average value of 11.9 ‰. This average is misleading because most of data range from between -2.1 and 4.5 ‰. However, due the lack of data, the distribution on the frequency histogram may not reflect the true distribution of δ^{34} S within the aquifer.

Ranges for δ^{34} S in various natural systems (atmosphere, fresh waters, marine evaporites, and sulfide in sedimentary rocks), as well as ranges for Permian, Pennsylvanian, and Mississippian age sulfates, are also shown on figure 40. Sulfates in ancient marine evaporites range from +35 to around +8 ‰ (Anderson and Arthur, 1983). The glacial-drift material might have sulfates from a variety of ages and, therefore, have δ ³⁴S values over the whole range of ancient marine evaporites. Data distribution from figure 40 indicates that almost twelve of the twenty-two samples that have been analyzed for the glacial drift aquifer fall within an area that could be explained by a simple atmospheric or fresh water input source. Seven samples with values ranging between 15.4 and 40.14 could be from the dissolution of marine evaporites. One sample is too heavy to be accounted for by the dissolution of gypsum or the oxidation of pyrite. Therefore, another source of sulfate or some biochemical process, such as sulfate reduction, is indicated.

Figure 41 is a plot of dissolved sulfate versus δ^{34} S and shows two distinct patterns in the data. The first pattern shows that for several samples as sulfate is depleted the δ^{34} S becomes heavier. This is what might be expected if the microbiological reduction of sulfate was occurring in the system (Long and others, 1986). All the δ^{34} S values that fall along this trend of high sulfate and light δ^{34} S, to lower sulfate and heavy δ^{34} S, are samples that are from Bay County. The second pattern is a cluster of data with low concentrations of sulfate and light δ^{34} S values. Most of these data plot in the southern half of the study area (fig. 41). These samples are probably related to other sources of sulfate or have not undergone sulfate reduction for the same length of time as some of the waters in Bay County. Not all data follow the first pattern indicating that sulfate reduction



Figure 40.—Frequency histogram of δ 34S from water in the glacial drift aquifer. Also shown are ranges for δ 34S in various natural systems as well as ranges for Permian, Pennsylvanian, and Mississippian age sulfates. The bulk of the data for atmosphere and sulfide in sedimentary rocks is in the rectangles.



Figure 41.—Plot showing the relationship between δ34S and dissolved sulfate from water in the glacial drift aquifer.

may be occurring in local areas. This is consistent with the conclusion of Long et al, (1988) that sulfate reduction was taking place in various parts of the aquifer for different lengths of time, creating the differing degrees of isotopic enrichment and sulfate depletion.

Chapter 8

SUMMARY AND CONCLUSIONS

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SUMMARY

Geochemical distribution maps from the glacial drift aquifer show that ground water has high dissolved-solids concentrations (> 1,000 mg/L) and high chloride concentrations (> 100 mg/L) in the Saginaw Bay Area. Ground water found throughout the rest of the aquifer has low dissolved solids and chloride concentrations. The distribution of data on Piper plots shows a cation trend from Ca dominant at low dissolved solids to Na dominant at high dissolved solids. The data also show an anion trend from HCO₃+CO₃-SO₄ dominant solutions at low dissolved solids to HCO₃+CO₃-Cl-SO₄ dominant solutions at intermediate dissolved solids to Cl-SO₄ dominant solutions at high dissolved solids. These trends are indicative of a mixing of water masses of various compositions. There are four major hydrochemical facies observed in the glacial drift aquifer: Ca-HCO₃, Na-Cl, Ca-SO₄, and Na-HCO₃. The predominant hydrochemical facies is Ca-HCO₃ with water from the Saginaw Bay Area dominated by a Na-Cl facies.

Geochemical modeling indicates that the source of solutes to the dilute waters of the glacial drift aquifer can be explained by water-rock interactions in the glacial deposits. Saturation index data suggest that most of the ground water in the study area is in equilibrium with aragonite, chalcedony, and quartz; undersaturated with respect to gypsum and slightly undersaturated with respect to dolomite. The ground water was also shown to have the potential to be in thermodynamic equilibrium with the clay minerals illite and kaolinite. Clay minerals such as chlorites and smectites may also affect water chemistry, but to what degree is uncertain. The solutes in the dilute water of the aquifer (dissolved solids < 750 mg/L) are believed to be controlled dominantly by water-rock interaction. It has been hypothesized that a significant amount of water-rock interaction takes place in the glacial drift aquifer prior to water entering the Grand River-Saginaw or underlying aquifers (Wahrer et al., 1993; Meissner, et al., 1993). Nearly all the water

entering the study area must initially go through the glacial-drift deposits and reacts with the various mineral constituents and becomes less reactive or in equilibrium with certain minerals before entering the underlying aquifers. The SI results from modeling waters in the Marshall aquifer (Meissner, et al., 1993) and the Grand River-Saginaw aquifer (Wahrer et al., 1993; Meissner, 1993) indicates very similar results with the SI data from the glacial drift aquifer.

It has been hypothesized that the source of the saline water in the SLA is from the upward advection or diffusion of fluids from below. The results from the frequency histogram of Cl/Br ratios from the glacial drift aquifer indicates that the major source of Cl to the aquifer is most likely a brine than from the dissolution of halite. The distribution of data on log-log plots indicates that the source for the high dissolved solids in the glacial drift aquifer is related to the concentrated waters of the Grand River-Saginaw, Parma-Bayport and Marshall aquifers. However, there doesn't seem to be any indication that the most concentrated waters of the Marshall are mixing with water in the glacial drift. The mixing appears to be with waters from the Parma-Bayport and Grand River-Saginaw aquifers. Log-log plots identified that the distribution of data from the glacial drift aquifer was similar to the distribution of data from the near-surface bedrock aguifers. The data distribution from the ion:Cl and ion:Br diagrams indicate that the most concentrated waters from all of the aquifers have a very similar distribution and the source of solutes may be related. These diagrams also indicate that there are two end member waters; a saline end member, and a dilute end member, as well as mixed waters. Mixing between these two end member waters could explain the distribution of high solutes observed in the glacial drift aquifer.

The chloride rich end member water is shown to be impacting the water chemistry of a portion of the glacial drift aquifer as indicated by the dilution trend or mixing trend back from very concentrated waters of the Parma-Bayport and Marshall aquifers. The distribution from the ion:Cl diagrams indicate that the high concentrated solutes in the

glacial drift aquifer and the near-surface-bedrock aquifers were similar and that the fluid was concentrated to past halite precipitation and had been enriched in calcium and depleted in magnesium, potassium, and sulfate with respect to the seawater evaporation curve.

The dilute end member waters of the glacial drift aquifer generally plot as a scattered distribution that suggests these waters are probably isolated from the interaction with the brine or concentrated waters of the underlying aquifers. This distribution also indicates that the ground water has several sources of solutes. The source for most of these solutes is probably derived from water-rock interactions that take place in the glacial drift. The glacial-drift deposits consist of a wide range of minerals that could contribute to the dissolved-solids concentrations. This interpretation is supported by the results of the chemical modeling The ion:Cl diagrams (figs. 28 - 33) also indicate that brine from the Pennsylvanian and Mississippian aquifers are chemically similar which makes it difficult to decern which brine may be affecting ground water in the glacial drift aquifer. The interaction between infiltrating meteoric water into the glacial drift aquifer and mixing with the concentrated water of the Grand River-Saginaw and Parma-Bayport aquifers could produce the water chemistry that is present.

Analysis of the relation between δD and $\delta^{18}O$ for the water in the glacial drift aquifer indicates that recent meteoric (post-glacial), glacial-age meteoric, and mixtures of these waters are present within the aquifer. Data distributions indicate in the Saginaw Bay Area isotopically light (-11.0 to -18.8) water is present. This is the same area that has high dissolved chloride concentrations. Work by Long and others (1993) showed that mixing of freshwater (modern and "glacial" meteoric) with various amounts of brine can account for the chloride concentrations and $\delta^{18}O$ signatures of ground water found in the study area. The distribution of $\delta^{18}O$ throughout the aquifer, also indicates a north-south gradient that reflects the climatic differences in the study area. The origin of the isotopically light ground water is most likely from water recharged into the basin from

glacial meltwater (Long and others, 1988, 1993). The isotopically light water is able to retain its isotopic signature due to the slow flushing of the system by present day recharge water. During the Pleistocene, ice lobes could have recharged ground-water into the basin from glacial meltwater in the SLA. The existence of the impermeable clays in conjunction with the regional discharge would enable these waters to show a very high negative value while also mixing with more concentrated waters from below (Long and others, 1993). Areas that were not covered by these thick clay sediments would have had water with highly negative isotopic values flushed out or diluted by more recent heavy isotopic meteoric water.

Eight ground water samples have been measured for ¹⁴C from the glacial drift aquifer with values ranging from 1.80 to 76.49. Figure 42 is a distribution map of the ¹⁴C values and indicates that the very low values of ¹⁴C are found in the SLA while the high values are located in the upland areas. A low ¹⁴C concentration may indicate that we are looking at relatively "old" water, while a high ¹⁴C concentration may indicate that we are looking relatively "young" water. This distribution of data is consistent with the concept of ground water recharge in the Upland Areas and ground water discharge in the Lowland Areas. The interpretations of the geochemical and isotopic data from the glacial drift aquifer are consistent with the proposed ground-water flow system for the Michigan basin and may put constraints on the flow models for the regional hydrology of the basin. Further investigations into the geochemistry of the basin aquifers may yield more information and a better understanding of the entire system.

Records from the 1890's show that a number of areas in the state have highly mineralized and saline water in the drift, as well as bedrock aquifers. Many of the reports precede the coal mining activity, which took place from 1897 to 1950. This suggests that the highly saline ground waters of the SLA are at least in part from natural processes. Subsurface activities, such as coal mining and disposal of brines associated with the exploration for oil, gas and brine, may have also affected the ground waters in select areas.



Figure 42.—Map showing the distribution of δ 14C in water from the glacial drift aquifer.

However, the exploration activities may have only enhanced the natural process of upwelling of brine in the SLA by providing conduits for the saline waters to move up and mix with the freshwater in the overlying aquifers. Therefore, in localized areas the drilling and mining activities of man may have sped up the natural process of upward migration of brine from below.

CONCLUSIONS

The goal of this study was to investigate the geochemistry and source of solutes in ground water from the glacial drift aquifer and to examine several hypotheses based on previous work by Long and others (1986, 1988, 1993) in the Michigan basin. There are 8 major conclusions reached in this thesis.

(1) There are two main processes controlling solute chemistry in the glacial drift aquifer.

1)Mixing with more concentrated fluids from underlying aquifers is occurring closer to the Saginaw Bay area. This area has been identified as a regional discharge area.

2)Water-rock interaction taking place mainly with ground water having low dissolved-solids concentrations.

(2) There is a continuum in the distribution of the data on the log-log diagrams. The data from the glacial drift aquifer plot in a similar area as the data for the Grand River-Saginaw, Parma-Bayport, and Marshall aquifers. The dissolvedsolids concentrations also become more concentrated with depth; glacial drift aquifer< Grand River-Saginaw< Parma-Bayport < Marshall aquifer.

(3) There is meteoric water in the glacial drift aquifer with light to heavy $\delta^{18}O$ and δD values indicating mixing between glacial-age meteoric water and modern meteoric water. (4) A north-south variation in δ^{18} O and δD exists in the glacial drift aquifer and is due to latitude.

(5) The SLA has high dissolved-solids concentrations (eg. Cl) and light δ^{18} O and δ D values. This area is also characterized by the presence of impermeable sediments.

(6) δ^{13} C values indicate that there is probably several sources of carbon to the aquifer.

(7) δ^{34} S values indicate that the heaviest values are found in the SLA and that sulfate reduction is occurring in parts of the SLA

(8) ¹⁴C relative age distribution is consistent with a model in which ground water is recharged in the upland areas and recharges in the lowland areas. Therefore, the water in the lowland areas would be older than the water in the recharge areas.

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